Inorg. Chem. **1994**, *33*, 1709–1718

Synthesis, Structures, and the Redistribution and Skeletal Cleavage Reactions of Siloxane-Bridged Ferrocenophanes

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Received September 16, 1993®

The 1,3-disila-2-oxaferrocenophanes $Fe(\eta^5\text{-}C_5H_4)_2(SiR_2)_2O$ (**1**) (**a**, R = Me; **b**, R = Ph), the 1,3,5-trisila-2,4-dioxaferrocenophane $Fe(\eta^5\text{-}C_5H_4)_2(SiMe_2O)_2SiMe_2$ (**2**), and the 1,3,5,7-tetrasila-2,4,6-trioxaferrocenophane $Fe(\eta^5\text{-}C_5H_4)_2(SiMe_2O)_3SiMe_2$ (**3**) have been prepared in low to good yield from the reaction of the appropriate α,ω-dichlorooligosiloxane $Cl(SiR_2O)_xSiR_2Cl$ (R = Me or Ph) with dilithioferrocene–tetramethylethylenediamine. The methylated species **1a**, **2**, and **3** were found to undergo redistribution and skeletal cleavage reactions rather than ring-opening polymerization when heated in the melt at elevated temperatures in the presence of small quantities of $K[OSiMe_3]$. Similar reactions were detected for **2** in solution in the presence of $K[OSiMe_3]$ or triflic acid as initiator and in attempts to copolymerize **2** with either the cyclotrisiloxane $[Me_2SiO]_3$ or the [1]ferrocenophane $Fe(\eta^5\text{-}C_5H_4)_2SiMe_2$. Analysis of the reaction products by ^{29}Si NMR and mass spectrometry showed that varying amounts of other siloxane-bridged [*n*]ferrocenophanes were formed together with cyclic and oligomeric siloxanes, small quantities of the linear species $Fc(SiMe_2O)_xSiMe_2Fc$ (**4**) ($Fc = Fe(\eta^5\text{-}C_5H_4)(\eta^5\text{-}C_5H_5)$, $x = 1\text{–}3$), and ferrocene. In contrast to the behavior of **1a**, **2**, and **3**, no redistribution reactions were detected for the more sterically encumbered phenylated 1,3-disila-2-oxaferrocenophane **1b** under similar conditions. In order to examine structural trends as the ring size and the substituents are varied the molecular structures of **1a**, **1b**, **2**, and **3** were determined by single-crystal X-ray diffraction. Because of the short siloxane bridge present, the cyclopentadienyl carbon–silicon bonds in **1a** and **1b** are almost eclipsed. In contrast, in **2** and **3** the presence of a longer siloxane bridge allows the cyclopentadienyl ligands in the ferrocenyl moiety to rotate relative to one another, which permits the adoption of a more stable staggered conformation. Crystals of **1a** are triclinic, space group $P\bar{1}$ with $a = 8.5893(14)$ Å, $b = 15.703(2)$ Å, $c = 19.098(4)$ Å, $\alpha = 69.684(13)°$, $\beta = 77.860(15)°$, $\gamma = 74.889(11)°$, $V = 2311.5(12)$ Å^3, and $Z = 6$. Crystals of **1b** are orthorhombic, space group $P2_12_12_1$ with $a = 10.782(2)$ Å, $b = 13.006(3)$ Å, $c = 20.082(4)$ Å, $V = 2816.1(14)$ Å^3, and $Z = 4$. Crystals of **2** are triclinic, space group $P\bar{1}$ with $a = 9.0693(6)$ Å, $b = 14.2473(9)$ Å, $c = 17.3733(10)$ Å, $\alpha = 68.004(5)°$, $\beta = 86.027(5)°$, $\gamma = 75.733(5)°$, $V = 2016.6$ (2) Å^3, and $Z = 4$. Crystals of **3** are monoclinic, space group $P2_1/c$, with $a = 13.521(5)$ Å, $b = 18.035(5)$ Å, $c = 20.265(5)$ Å, $\beta = 94.010(2)°$, V = 4930(3) Å^3, and $Z = 8$.

Introduction

The development of new routes to polymers which contain inorganic elements in the main chain represents a synthetic challenge of growing interest.[1] Ring-opening polymerization (ROP), which is a powerful route to organic polymers, represents an emerging methodology for the preparation of these materials.[2–7] Cyclic siloxanes provide an excellent example of a well-studied, polymerizable inorganic ring system, and the ROP of species such as $[Me_2SiO]_x$ (x = 3 or 4) represents the most important current route to high molecular weight polysiloxanes (silicones).[3] As part of our general program directed at developing ROP as a route to polymeric materials containing main group elements[4,5] or transition metals[6,7] in the main chain we are investigating cycloheterosiloxanes.[8] These interesting cyclic species contain skeletal silicon and oxygen atoms together with other heteroatoms or heterofragments.[8,9] Although a variety of cycloheterosiloxanes have been reported and structurally characterized, very few attempts to polymerize these species have been described.[10,11]

Recently we reported the synthesis and studies of the structure and polymerization behavior of a series of cyclic borasiloxanes.[5] Using conditions under which cyclic siloxanes polymerize, these species were found to be resistant to ROP and instead preferentially underwent ring–ring transformation reactions to yield

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® Abstract published in *Advance ACS Abstracts*, March 1, 1994.

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0020-1669/94/1333-1709$04.50/0

mainly larger borasiloxane rings containing a single boron atom, together with cyclic and polymeric siloxanes and the boroxine $[PhBO]_3$.[5] These studies indicated that the formation of cycloboroxine presents a significant thermodynamic barrier to poly(borasiloxane) formation using ring-opening methods. We therefore turned our attention to the incorporation of other elements and moieties into the cyclic siloxane ring structure and studies of the polymerization behavior of these species. The recent discovery of the ROP of strained, ring-tilted [1]- and [2]-ferrocenophanes to yield high molecular weight organometallic polymers[6,7] prompted us to investigate siloxane rings which incorporate ferrocenyl units. In this paper we report full details of our studies on the structures and polymerization behavior of a series of siloxane-bridged [*n*]ferrocenophanes.

Results and Discussion

Synthesis and Characterization of the [3]Siloxanylferrocenophanes 1a and 1b. In order to investigate the polymerization behavior of siloxane-bridged [*n*]ferrocenophanes, a range of species with different substituents and ring sizes was synthesized and characterized. Several species of this type have been previously reported.[10,11] In particular, compound **1a** has been previously prepared via the reaction of the ferrocenyldisilane $Fe(\eta^5\text{-}C_5H_4)_2(SiMe_2)_2$ with HCl/EtOH[12a] and also via the hydrolysis of $Fe(\eta^5\text{-}C_5H_4SiMe_2OEt)_2$.[10b] In our work the 1,3-disila-2-oxaferrocenophanes **1a** and **1b** were prepared via the reaction of dilithioferrocene–tetramethylethylenediamine with the dichlorodisiloxanes $ClR_2SiOSiR_2Cl$ (R = Me or Ph) (Scheme 1). The products were isolated as yellow-orange crystalline materials in low yield (8–18%). An alternative synthesis of **1a** was developed involving the reaction of dilithioferrocene–tetramethylethylenediamine with excess dimethyldichlorosilane to yield $Fe(\eta^5\text{-}C_5H_4SiMe_2Cl)_2$, followed by hydrolysis. However, the yield of **1a** after purification by column chromatography was similarly low (ca. 13%). Compounds **1a** and **1b** were characterized by ^{29}Si and ^1H NMR, mass spectrometry, and X-ray crystallography. The ^{29}Si NMR spectrum of **1a** (in $CDCl_3$) consisted of a singlet resonance at 1.1 ppm, which is at slightly lower field than that of $[Me_2SiO]_3$ ($\delta = -9.0$ ppm). The ^{29}Si NMR resonance of **1b** ($\delta = -15.4$ ppm) was also shifted to slightly lower field compared to that of the cyclosiloxane counterpart ($[Ph_2SiO]_3$, $\delta = -33.0$ ppm). The mass spectra of **1a** and **1b** showed the presence of molecular ions and intense peaks arising from logical fragmentation products. These crystalline compounds are unaffected by atmospheric moisture and are stable to hydrolysis when dissolved in moist solvents.

To the best of our knowledge, no structural data on siloxane-bridged [*n*]ferrocenophanes has been published to date. Thus, in order to examine the structural effects of incorporating a ferrocene group into a siloxane ring and to compare the molecular structures of **1a** and **1b**, an X-ray diffraction study of a single crystal of each compound was undertaken.

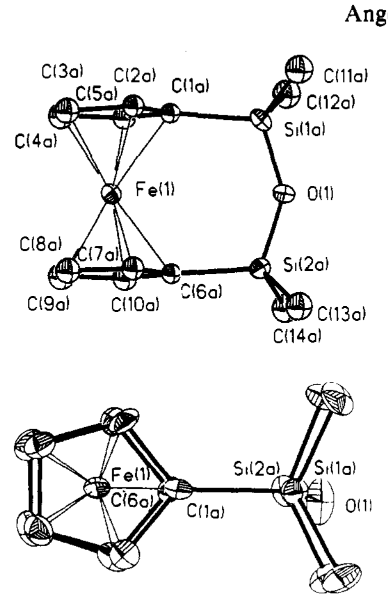
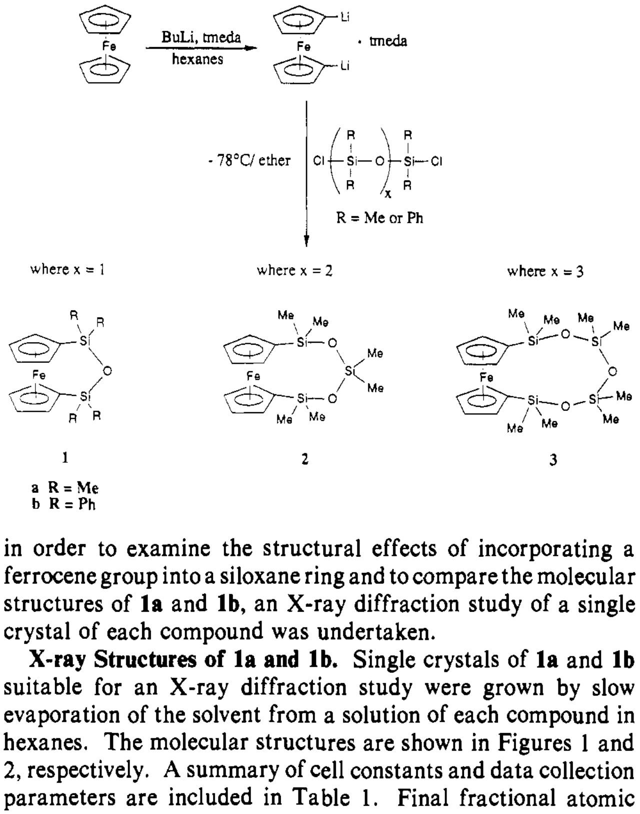


Figure 1. (a) Top: Molecular structure of **1a** (isomer A). (b) Bottom: Alternate view of a molecule of **1a** (isomer A).

Scheme 1



X-ray Structures of 1a and 1b. Single crystals of **1a** and **1b** suitable for an X-ray diffraction study were grown by slow evaporation of the solvent from a solution of each compound in hexanes. The molecular structures are shown in Figures 1 and 2, respectively. A summary of cell constants and data collection parameters are included in Table 1. Final fractional atomic coordinates and selected bond lengths and angles for **1a** and **1b** are given in Tables 2 and 3 for **1a** and Tables 4 and 5 for **1b**, respectively.

The X-ray diffraction studies confirmed that both **1a** and **1b** possess a ferrocene unit with each cyclopentadienyl group linked by a three atom Si–O–Si bridge. In the case of **1a** three structurally distinct molecules (A, B, and C) were found in the crystal which differ only slightly in the conformation of the siloxane-bridged ferrocenophane ring. In contrast, only one structurally distinct molecule was found for **1b**. The existence of the three different molecules for **1a** can be attributed to the high conformational flexibility of the Si–O–Si linkage in this compound which allows molecules of **1a** to exist as several different conformers that possess virtually the same energy and can easily interconvert. In compound **1b**, which possesses more bulky phenyl substituents at silicon, less conformational flexibility probably

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Table 1. Summary of Crystal Data and Intensity Collection Parameters

	1a	**1b**	**2**	**3**
formula	$C_{14}H_{20}FeOSi_2$	$C_{34}H_{28}FeOSi_2$	$C_{16}H_{26}FeO_2Si_3$	$C_{18}H_{32}FeO_3Si_4$
M_r	316.3	564.6	390.5	462.64
cryst class	triclinic	orthorhombic	triclinic	monoclinic
space group	$P\bar{1}$	$P2_12_12_1$	$P\bar{1}$	$P2_1/c$
temp, K	294	294	294	294
a, Å	8.5893(14)	10.782(2)	9.0693(6)	13.521(5)
b, Å	15.703(2)	13.006(3)	14.2473(9)	18.035(5)
c, Å	19.098(4)	20.082(4)	17.3733(10)	20.265(5)
α, deg	69.684(13)		68.004(5)	
β, deg	77.860(15)		86.027(5)	94.010(2)
γ, deg	74.889(11)		75.733(5)	
V, Å^3	2311.5(12)	2816.1(14)	2016.6(2)	4930(3)
Z	6	4	4	8
D_{calcd}, g cm^{-3}	1.363	1.332	1.286	1.252
μ(Mo Kα), mm^{-1}	1.120	0.646	0.929	0.820
λ(Mo Kα), Å	0.710 73	0.710 73	0.710 73	0.709 30
R_{int}, %	4.58		3.37	4.02
R,[a] %	5.64	4.19	3.46	4.32
R_w*,[a] %	7.43	4.98	4.55	4.16
abs cor	0.7610/1.2030	0.8140/1.1590	0.703/0.656	0.7940/1.3790

[a] Definition of R factors: $R = \Sigma(\text{del})/\Sigma(F(\text{obs}))$. $R_w = [\Sigma(\text{weight} \times \text{del})^2/\Sigma(\text{weight} \times F(\text{obs})^2)]^{1/2}$, where del $= [F(\text{obs}) - F(\text{calc})]$.

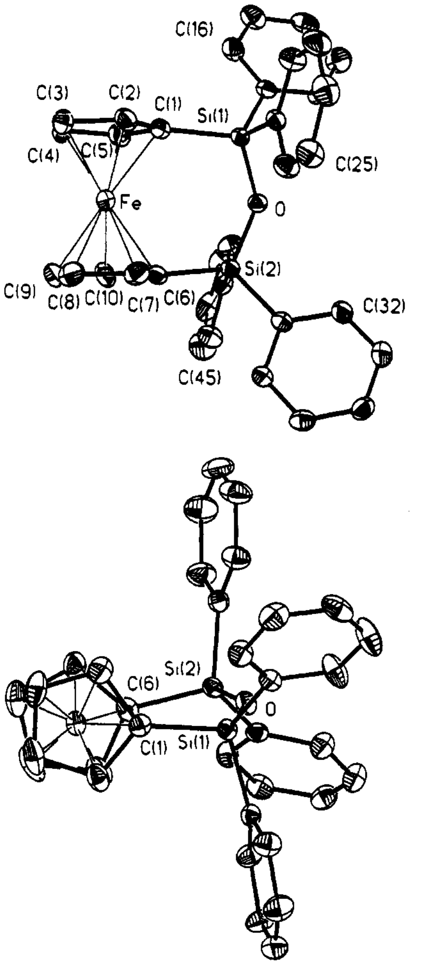

Figure 2. (a) Top: Molecular structure of **1b**. (b)Bottom: Alternate view of a molecule of **1b**.

exists and so only one conformer is found. The cyclopentadienyl ligands in each isomer of **1a** and in **1b** are virtually planar and parallel to one another. Thus, no cyclopentadienyl carbon atom shows a mean deviation from the plane greater than 0.02 Å in the isomers of **1a** and 0.01 Å in **1b**. In addition, the tilt angles between the planes of the cyclopentadienyl ligands are not greater than 2.5(12)° for any of these molecules. The bond angles and bond lengths within the cyclopentadienyl ligands of the molecules of **1a** and **1b** are normal. The angles between the two ipso carbon–silicon bonds projected on the mean plane of the cyclopentadienyl ligands are, respectively, 0.6(12), 5.2(12), and 2.1(12)° for the three molecules of **1a**. The corresponding value for **1b** is 13.6(5)°. These values indicate that the relatively short siloxane bridge present in these compounds enforces virtually eclipsed conformations for the cyclopentadienyl ligands and the side groups attached to the silicon atoms (see Figures 1b and 2b). The Si–O–Si bond angles for the three molecules of **1a** are 143.1(7), 144.5 (7), and 142.1(6)° and the corresponding value for **1b** is 139.8(2)°. These values are significantly greater than values found in $[Me_2SiO]_3$ (125.0(5)°)[14a] and $[Ph_2SiO]_3$ (131.8(8)°)[14b] which indicates that **1a** and **1b** are substantially less strained than siloxane six-membered rings. However, the Si–O–Si angles for **1a** and **1b** are smaller than the values found in $[Ph_2SiO]_4$ (152.3(2) and 167.4(2)°)[14c] and $Me_3SiOSiMe_3$ (148.8(1)°),[14d] which suggests that a very small amount of strain is probably present. Further evidence for the presence of a small degree of strain in **1a** and **1b** is provided by the slight distortion from planarity at the cyclopentadienyl carbon atom bonded to silicon. This is illustrated by the values of the angles, β, between the plane of the cyclopentadienyl ligand and the C–Si bond, which deviate slightly from zero. For **1a** the average β values are 4.1(7), 4.5(8), and 3.3(8)° for the three conformers present. For **1b** the corresponding average value of β is 4.5(3)°. The Si–O bond lengths in **1a** and **1b** vary from 1.59(2) to 1.62(2) Å and are on average slightly shorter than in $[Ph_2SiO]_3$ where the corresponding average value is 1.64(1) Å.[14b] The other structural features of **1a** and **1b** are normal.

It is interesting to compare the structure of the 1,3-disila-2-oxaferrocenophanes **1a** and **1b** with that of the 1,2-disilaferrocenophane $[Fe(\eta^5\text{-}C_5H_4)_2(SiMe_2)_2]$, which contains a disilane bridge.[6c] In the latter species the shorter bridge leads to a slightly greater tilt angle (4.19(2)°) between the planes of the cyclopentadienyl ligands. In addition, the distortion from planarity at the ipso carbon atoms of the cyclopentadienyl ligands bonded to silicon is greater with an average value of β of 10.8(3)°. This suggests that **1a** and **1b** are less strained than $[Fe(\eta^5\text{-}C_5H_4)_2(SiMe_2)_2]$. However, the structures of **1a** and **1b** differ much more dramatically from those of [1]ferrocenophanes with one silicon atom in the bridge which are highly strained and

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Table 2. Final Fractional Atomic Coordinates and Equivalent Isotropic Displacement Coefficients (Å^2) for the Non-Hydrogen Atoms of **1a**

atom	x	y	z	U_{eq}^{a}
Fe(1A)	0.3651(2)	0.2131(1)	0.8470(1)	0.032(1)
Si(1A)	−0.0035(4)	0.3617(3)	0.8157(2)	0.040(2)
Si(2A)	0.0224(4)	0.1622(3)	0.8191(2)	0.043(1)
O(1)	−0.0402(11)	0.2729(6)	0.8034(6)	0.063(6)
C(1A)	0.2110(14)	0.3403(9)	0.8332(7)	0.031(6)
C(2A)	0.3490(15)	0.3489(9)	0.7801(8)	0.040(7)
C(3A)	0.4934(16)	0.3169(11)	0.8145(8)	0.050(8)
C(4A)	0.4383(17)	0.2927(11)	0.8945(8)	0.054(8)
C(5A)	0.2681(16)	0.3076(11)	0.9047(7)	0.050(7)
C(6A)	0.2367(14)	0.1266(9)	0.8360(7)	0.035(6)
C(7A)	0.3793(16)	0.1322(10)	0.7817(8)	0.046(7)
C(8A)	0.5182(15)	0.1019(10)	0.8195(9)	0.052(8)
C(9A)	0.4671(17)	0.0769(11)	0.8982(9)	0.056(8)
C(10A)	0.2968(15)	0.0912(10)	0.9084(8)	0.046(7)
C(11A)	−0.0414(18)	0.4595(10)	0.7283(8)	0.063(8)
C(12A)	−0.1428(15)	0.3900(11)	0.8950(8)	0.062(8)
C(13A)	−0.003(17)	0.1399(11)	0.7333(7)	0.060(8)
C(14A)	−0.1036(16)	0.1006(13)	0.9015(8)	0.069(9)
Fe(2)	0.2964(2)	0.2775(2)	0.4959(1)	0.038(1)
Si(1B)	0.6698(5)	0.1293(3)	0.5102(3)	0.047(2)
Si(2B)	0.6446(4)	0.3229(3)	0.5238(2)	0.041(2)
O(2)	0.7151(11)	0.2172(9)	0.5208(2)	0.091(7)
C(1B)	0.4572(17)	0.1544(10)	0.4916(8)	0.045(7)
C(2B)	0.3140(17)	0.1389(10)	0.5451(9)	0.054(8)
C(3B)	0.1764(18)	0.1762(12)	0.5096(10)	0.061(9)
C(4B)	0.2254(19)	0.2180(13)	0.4319(10)	0.068(10)
C(5B)	0.3942(19)	0.2073(11)	0.4207(9)	0.057(8)
C(6B)	0.4235(13)	0.3564(10)	0.5178(7)	0.033(6)
C(7B)	0.2926(16)	0.3354(10)	0.5756(8)	0.045(7)
C(8B)	0.1789(15)	0.4133(10)	0.4699(8)	0.047(7)
C(9B)	0.1471(16)	0.3695(10)	0.5463(8)	0.044(7)
C(10B)	0.3513(16)	0.4068(10)	0.4501(7)	0.042(7)
C(11B)	0.6947(20)	0.0312(12)	0.5974(9)	0.088(10)
C(12B)	0.8117(18)	0.1008(14)	0.4313(9)	0.084(10)
C(13B)	0.6793(18)	0.3279(11)	0.6146(7)	0.063(8)
C(14B)	0.7533(17)	0.4018(13)	0.4425(9)	0.079(10)
Fe(3)	0.0785(2)	0.2380(2)	0.1510(1)	0.037(1)
Si(1C)	−0.3029(5)	0.3748(3)	0.1702(2)	0.040(2)
Si(2C)	−0.2900(4)	0.1766(3)	0.1710(2)	0.040(2)
O(3)	−0.3569(10)	0.2778(8)	0.1845(7)	0.071(6)
C(1C)	−0.0788(16)	0.3534(10)	0.1636(8)	0.046(7)
C(2C)	0.0204(17)	0.3193(11)	0.2188(9)	0.059(8)
C(3C)	0.1874(19)	0.3141(12)	0.1866(12)	0.077(11)
C(4C)	0.1940(18)	0.3478(11)	0.1073(10)	0.065(9)
C(5C)	0.0293(17)	0.3777(11)	0.0919(10)	0.063(9)
C(6C)	−0.0630(15)	0.1450(9)	0.1590(7)	0.033(6)
C(7C)	0.0363(16)	0.1092(9)	0.2168(8)	0.041(7)
C(8C)	0.2043(18)	0.1041(10)	0.1823(8)	0.055(8)
C(9C)	0.2060(15)	0.1358(11)	0.1045(9)	0.054(8)
C(10C)	0.0408(14)	0.1629(10)	0.0892(8)	0.044(7)
C(11C)	−0.3994(19)	0.4148(12)	0.2520(8)	0.077(9)
C(12C)	−0.3774(19)	0.4601(12)	0.0826(8)	0.080(9)
C(13C)	−0.3768(18)	0.0929(12)	0.2535(9)	0.075(10)
C(14C)	−0.3622(16)	0.1818(12)	0.0859(8)	0.066(9)

^{a} Equivalent isotropic U defined as one-third of the trace of the orthogonalized U_{ij} tensor.

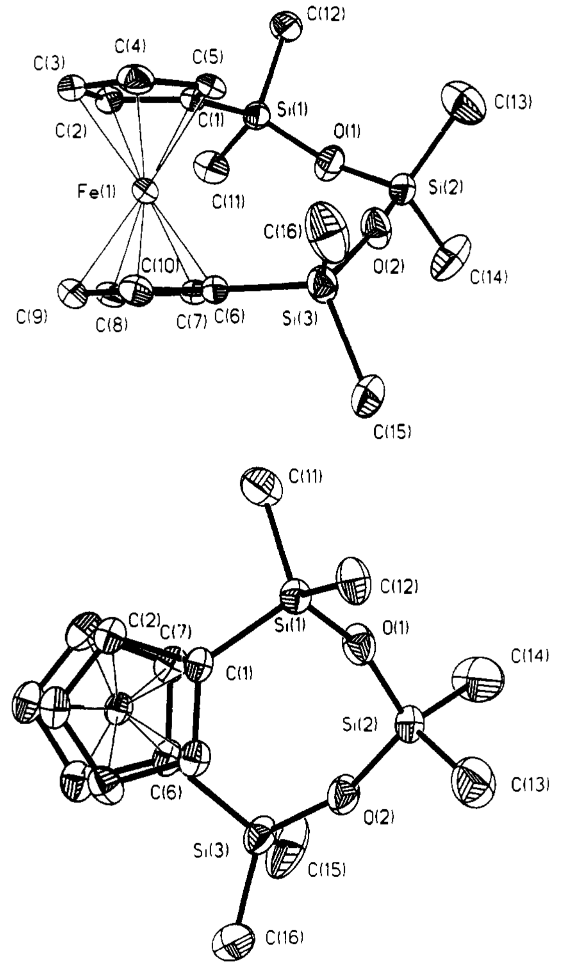

Figure 3. (a) Top: Molecular structure of **2** (isomer A). (b) Bottom: Alternate view of a molecule of **2** (isomer A).

possess tilt-angles between the planes of the cyclopentadienyl ligands of ca. 21° and β angles of up to ca. 41°.[6c,15]

Synthesis and Characterization of the 1,3,5-Trisila-2,4-Dioxaferrocenophane 2 and the 1,3,5,7-Tetrasila-2,4,6-trioxaferrocenophane 3. In order to study compounds containing larger siloxane-bridged ferrocenophane rings the species **2** and **3** were prepared via the reaction of dilithioferrocene–tetramethylenediamine with the appropriate α,ω-dichlorosiloxanes $ClMe_2Si(OSiMe_2)_nCl$ (n = 2 or 3) (Scheme 1). These amber crystalline compounds were isolated, purified, and characterized in an analogous manner to **1a** and **1b**. For example, the ^{29}Si NMR spectrum of **2** (in $CDCl_3$) consisted of two singlet resonances at $\delta = -0.5$ and -21.9 ppm with relative intensities 2:1. The chemical shift of the former resonance is similar to that for **1a** and was therefore assigned to the silicon atom bonded to the cyclopentadienyl ligand. The ^{29}Si NMR spectrum of **3** (in $CDCl_3$) consisted of two equal intensity singlet resonances at $\delta = 0.0$ and -20.4 ppm with the former assigned to the silicon atoms bonded to the cyclopentadienyl ligand for similar reasons. In the cases of both **2** and **3** the higher field ^{29}Si NMR resonance assigned to the silicon atom furthest removed from the ferrocenyl unit possesses a chemical shift quite similar to that for the linear polysiloxane $[Me_2SiO]_n$ ($\delta = -21.5$ ppm) which suggests that very little strain is present in these compounds. ^1H NMR and elemental analysis data for **2** and **3** were also consistent with the assigned structures.

In order to provide complete structural characterization of **2** and **3** and to allow comparison with related species **1a** and **1b** which possess smaller siloxane-bridged ferrocenophane rings, each was characterized by a single crystal X-ray diffraction study.

X-ray Structures of 2 and 3. Single crystals of **2** and **3** were grown from a 1:1 mixture of hexanes and dichloromethane. The molecular structures are shown in Figure 3 and 4, respectively. A summary of cell constants and data collection parameters are included in Table 1. Final fractional atomic coordinates and selected bond lengths and angles for **2** and **3** are given in Tables 6 and 7 for **2**, and Tables 8 and 9 for **3**, respectively.

The X-ray diffraction studies confirmed that **2** and **3** possess a ferrocene unit with the cyclopentadienyl ligands linked by five- and seven-atom siloxane bridges, respectively. In a similar way to the case of **1a**, in each case two structurally distinct molecules (A and B) were found in the crystal which differed only slightly in the conformation of the siloxane-bridged ferrocenophane rings.

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(15) See, for example: Stoeckli-Evans, H.; Osborne, A. G.; Whiteley, R. H. *Helv. Chim. Acta.* **1976**, *59*, 2402.

Table 3. Selected Bond Lengths and Angles for **1a** (Estimated Standard Deviations Given in Parentheses)

Bond Lengths (Å)					
Fe(1)–C(1A)	2.053(12)	Fe(3)–C(1C)	2.015(14)	Fe(2)–C(2B)	2.027(15)
Fe(1)–C(3A)	2.050(17)	Fe(3)–C(3C)	2.047(24)	Fe(2)–C(4B)	2.038(24)
Fe(1)–C(5A)	2.054(17)	Fe(3)–C(5C)	2.065(15)	Fe(2)–C(6B)	2.040(17)
Fe(1)–C(7A)	2.034(18)	Fe(3)–C(7C)	2.056(13)	Fe(2)–C(8B)	2.041(14)
Fe(1)–C(9A)	2.056(14)	Fe(3)–C(9C)	2.056(17)	Fe(2)–C(10B)	2.050(15)
Si(1A)–O(1)	1.609(13)	Si(1C)–O(3)	1.624(13)	Si(1B)–C(1B)	1.848(16)
Si(1A)–C(11A)	1.855(13)	Si(1C)–C(11C)	1.840(17)	Si(1B)–C(12B)	1.834(17)
Si(2A)–O(1)	1.617(10)	Si(2C)–O(3)	1.633(13)	Si(2B)–C(6B)	1.851(12)
Si(2A)–C(13A)	1.847(18)	Si(2C)–C(13C)	1.829(15)	Si(2B)–C(14B)	1.864(15)
C(1A)–C(2A)	1.931(16)	C(1C)–C(2C)	1.367(22)	C(1B)–C(5B)	1.452(21)
C(2A)–C(3A)	1.418(20)	C(2C)–C(3C)	1.430(21)	C(3B)–C(4B)	1.419(24)
C(4A)–C(5A)	1.402(19)	C(4C)–C(5C)	1.430(21)	C(6B)–C(7B)	1.417(17)
C(6A)–C(10A)	1.451(20)	C(6C)–C(10C)	1.422(17)	C(7B)–C(9B)	1.377(19)
C(8A)–C(9A)	1.417(22)	C(8C)–C(9C)	1.393(24)	C(8B)–C(10B)	1.435(18)
Fe(2)–C(1B)	2.079(14)	Fe(1)–C(2A)	2.056(12)	Fe(3)–C(2C)	2.025(19)
Fe(2)–C(3B)	2.029(20)	Fe(1)–C(4A)	2.053(20)	Fe(3)–C(4C)	2.049(17)
Fe(2)–C(5B)	2.023(18)	Fe(1)–C(6A)	2.046(16)	Fe(3)–C(6C)	2.079(16)
Fe(2)–C(7B)	2.016(18)	Fe(1)–C(8A)	2.050(15)	Fe(3)–C(8C)	2.040(13)
Fe(2)–C(9B)	2.034(15)	Fe(1)–C(10A)	2.031(14)	Fe(3)–C(10C)	2.052(19)
Si(1B)–O(2)	1.614(16)	Si(1A)–C(1A)	1.865(13)	Si(1C)–C(1C)	1.851(14)
Si(1B)–C(11B)	1.841(15)	Si(1A)–C(12A)	1.831(15)	Si(1C)–C(12C)	1.857(14)
Si(2B)–O(2)	1.629(14)	Si(2A)–C(6A)	1.842(13)	Si(2C)–C(6C)	1.868(12)
Si(2B)–C(13B)	1.851(17)	Si(2A)–14(A)	1.832(14)	Si(2C)–C(14C)	1.828(17)
C(1B)–C(2B)	1.439(19)	C(1A)–C(5A)	1.426(19)	C(1C)–C(5C)	1.473(21)
C(2B)–C(3B)	1.378(23)	C(3A)–C(4A)	1.444(19)	C(3C)–C(4C)	1.414(28)
C(4B)–C(5B)	1.394(22)	C(6A)–C(7A)	1.429(17)	C(6C)–C(7C)	1.406(20)
C(6B)–C(10B)	1.434(18)	C(7A)–C(8A)	1.413(21)	C(7C)–C(8C)	1.449(19)
C(8B)–C(9B)	1.383(19)	C(9A)–C(10A)	1.403(19)	C(9C)–C(10C)	1.433(19)
Bond Angles (deg)					
Si(1A)–O(1)–Si(2A)	143.1(7)	O(1)–Si(1A)–C(1A)	111.1(6)		
Si(1B)–O(2)–Si(2B)	144.5(7)	O(2)–Si(1B)–C(1B)	111.7(7)		
Si(1C)–O(3)–Si(2C)	142.1(6)	O(3)–Si(1C)–C(1C)	109.1(6)		

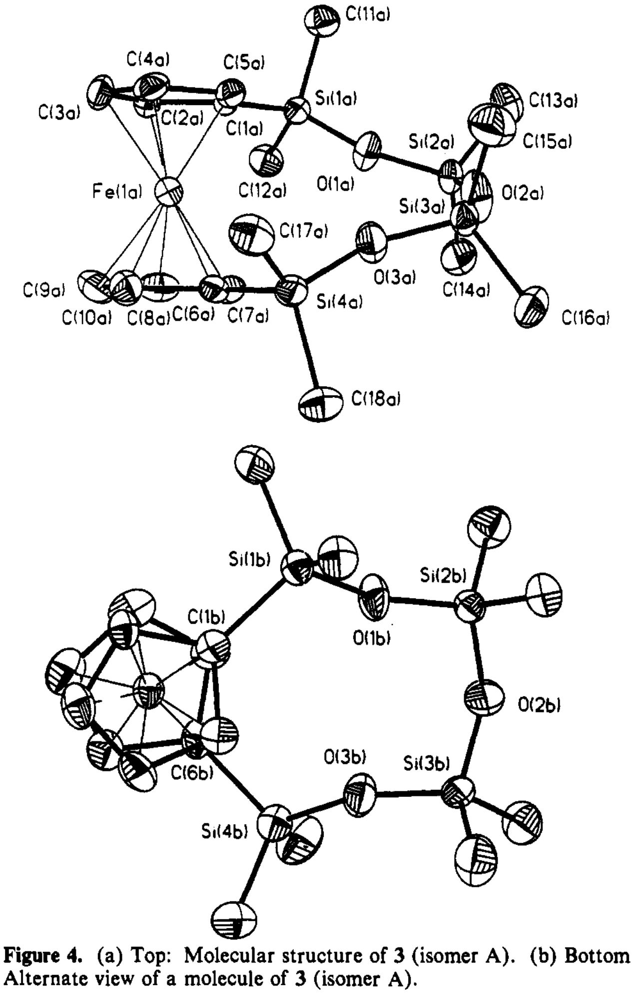


Figure 4. (a) Top: Molecular structure of **3** (isomer A). (b) Bottom: Alternate view of a molecule of **3** (isomer A).

The cyclopentadienyl ligands in each of the isomers of **2** and of **3** are virtually planar and parallel to one another. Thus, no cyclopentadienyl carbon atom shows a mean deviation from the plane greater than 0.01 Å in either compound. In addition, the tilt angles between the planes of the cyclopentadienyl groups are all less than 1.5(5)° for these molecules and the bond angles and bond lengths within the η-C_5H_4 ligands of the molecules of **2** and **3** are normal. The angles between the two ipso carbon–silicon projected on the mean plane of the cyclopentadienyl ligands are 73.9(5) and 71.8(5)° for each of the two isomers of **2** and 87.1(8) and 87.6(8)° for each of the two isomers of **3**. This indicates that the cyclopentadienyl ligands in **2** and **3** are significantly rotated relative to one another compared to the situation in **1a** where the corresponding angles are less than 6°. The degree of rotation increases in the order **1a** < **2** < **3** as the length of the siloxane bridge increases. The rotation of the cyclopentadienyl ligands relative to one another allows the siloxane-bridged ferrocenophane rings in **2** and **3**, to adopt a even more favorable and unstrained conformation than in **1a** and **1b**. For example, the methyl groups at silicon are no longer eclipsed in **2** and **3** which contrasts with the situation for **1a** . This can be appreciated by inspecting the views of the molecules shown in Figures 1b, 3b, and 4b. The Si–O–Si bond angles in **2** and **3** vary from 154.4(7) to 165.7(2)° and are significantly wider than those in **1a** and **1b** where the values vary from 139.8(2) to 144.5(7)° and are comparable to the values found in essentially unstrained cyclotetrasiloxanes such as $[Ph_2SiO]_4$ (152.3(2) and 167.4(2)°).[14c] This suggests than **2** and **3** are almost completely unstrained. Further evidence in favor of this conclusion is found by consideration of the geometry of the cyclopentadienyl carbon atom bonded to silicon. In **1a** and **1b** and strained [*n*]ferrocenophanes the angle between the plane of the cyclopentadienyl ligand and the C–Si bond deviates slightly but significantly from zero. However, in **2** and **3** the corresponding average values are very small (β_{av} = 1.5(2) and 1.7(2)° for the two molecules of **2** and β_{av} = 3.0(6) and 1.8(6)° for the two molecules of **3**). Other structural parameters for **2** and **3** are similar to those for **1a** and **1b** and are unexceptional.

Polymerization Behavior of the Siloxane-Bridged [*n*]ferrocenophanes 1a, 1b, 2, and 3. The ROP of cyclic siloxanes such as $[Me_2SiO]_3$ and $[Me_2SiO]_4$ in the presence of acid or base

Table 4. Final Fractional Atomic Coordinates and Equivalent Isotropic Displacement Coefficients (Å^2) for the Non-Hydrogen atoms of **1b** (Estimated Standard Deviations Given in Parentheses)

atom	*x*	*y*	*z*	U_{eq}[a]
Fe	0.3094(1)	0.8057(1)	0.12471(1)	0.044(1)
Si(1)	0.2309(1)	0.5889(1)	0.2106(1)	0.036(1)
Si(2)	0.5003(1)	0.6044(1)	0.1617(1)	0.036(1)
O	0.3774(3)	0.5605(3)	0.2000(2)	0.042(1)
C(1)	0.1986(5)	0.7244(3)	0.1883(2)	0.043(1)
C92)	0.1294(5)	0.7593(4)	0.1337(3)	0.054(2)
C(3)	0.1338(6)	0.8673(5)	0.1282(4)	0.075(2)
C(4)	0.2051(7)	0.9013(4)	0.1831(3)	0.073(2)
C(5)	0.2457(6)	0.8155(4)	0.2194(3)	0.059(2)
C(6)	0.4669(4)	0.7195(4)	0.1103(2)	0.043(2)
C(7)	0.3964(5)	0.7268(5)	0.0506(2)	0.059(2)
C(8)	0.3860(6)	0.8319(5)	0.0329(3)	0.072(2)
C(9)	0.4472(6)	0.8913(5)	0.0814(3)	0.074(3)
C(10)	0.4959(5)	0.8240(4)	0.1290(3)	0.061(2)
C(11)	0.1941(4)	0.5651(4)	0.2999(2)	0.041(1)
C(12)	0.2237(6)	0.4726(5)	0.3288(3)	0.071(2)
C(13)	0.1946(7)	0.4504(6)	0.3938(3)	0.087(3)
C(14)	0.1373(5)	0.5245(6)	0.4323(3)	0.068(2)
C(15)	0.1065(6)	0.6164(5)	0.4056(3)	0.069(2)
C(16)	0.1333(6)	0.6358(4)	0.3390(3)	0.059(2)
C(21)	0.1369(4)	0.5068(4)	0.1553(2)	0.069(2)
C(22)	0.0149(5)	0.4786(5)	0.1706(3)	0.066(2)
C(23)	−0.0573(5)	0.4260(5)	0.1264(3)	0.061(2)
C(24)	−0.0120(6)	0.3987(5)	0.0641(3)	0.053(2)
C(25)	0.1068(6)	0.4234(5)	0.0480(3)	0.039(1)
C(26)	0.1807(5)	0.4751(4)	0.0933(3)	0.054(2)
C(31)	0.5612(4)	0.4994(4)	0.1076(2)	0.061(2)
C(32)	0.5498(5)	0.3959(4)	0.1248(3)	0.054(2)
C(33)	0.5994(5)	0.3194(4)	0.0859(3)	0.061(2)
C(34)	0.6609(5)	0.3426(4)	0.0291(3)	0.053(2)
C(35)	0.6722(5)	0.4430(4)	0.0094(2)	0.052(2)
C(36)	0.6237(5)	0.5201(4)	0.0482(2)	0.047(2)
C(41)	0.6173(5)	0.6420(4)	0.2251(2)	0.042(1)
C(42)	0.5881(5)	0.6494(4)	0.2923(3)	0.057(2)
C(43)	0.6749(6)	0.6841(5)	0.3379(3)	0.076(2)
C(44)	0.7904(7)	0.7121(5)	0.3187(4)	0.082(3)
C(45)	0.8220(6)	0.7043(6)	0.2526(4)	0.089(3)
C(46)	0.7372(5)	0.6696(5)	0.2075(3)	0.062(2)

[a] Equivalent isotropic *U* defined as one-third of the trace of the orthogonalized $\mathbf{U}_{ij}$ tensor.

Table 5. Selected Bond Lengths and Angles for **1b** (Estimated Standard Deviations Given in Parentheses)

	Bond Lengths (Å)		
Fe–C(1)	2.045(5)	Si(2)–O	1.636(3)
Fe–C(2)	2.041(5)	Si(2)–C(6)	1.854(5)
Fe–C(3)	2.057(6)	Si(2)–C(31)	1.865(5)
Fe–C(4)	2.046(7)	Si(2)–C(41)	1.857(5)
Fe–C(5)	2.027(6)	C(1)–C(2)	1.402(7)
Fe–C(6)	2.036(5)	C(1)–C(5)	1.432(7)
Fe–C(7)	1.637(3)	C(2)–C(3)	1.410(8)
Fe–C(8)	2.048(6)	C(3)–C(4)	1.416(10)
Fe–C(9)	2.050(6)	C(4)–C(5)	1.403(8)
Fe–C(10)	2.027(6)	C(6)–C(7)	1.422(7)
Si(1)–O	1.636(3)	C(6)–C(10)	1.444(7)
Si(1)–C(1)	1.851(5)	C(7)–C(8)	1.417(9)
Si(1)–C(11)	1.862(4)	C(8)–C(9)	1.407(9)
Si(1)–C(21)	1.845(5)	C(9)–C(10)	1.397(9)
	Bond Angles (deg)		
Si(1)–O–Si(2)	139.8(2)	O–Si(2)–C(6)	112.8(2)
O–Si(1)–C(1)	111.5(2)		

catalysts is well-known and provides one of the main routes to polysiloxanes.[3] In order to explore the influence of a skeletal ferrocenyl unit on the polymerizability of siloxane rings we studied the behavior of **1a**, **1b**, **2**, and **3** using conditions under which conventional siloxanes polymerize. Polymerization experiments mainly involved reactions in the melt in the presence or absence of added base initiators. However, selected experiments in solution were also carried out. Two strategies to induce copolymerization were also examined.

Table 6. Final Fractional Coordinates (× 10^4) and Equivalent Isotropic Displacement Coefficients (Å^2 × 10^3) for the Non-Hydrogen Atoms of **2** (Estimated Standard Deviations are in Parentheses)

atom	*x*	*y*	*z*	U_{eq}[a]
Fe(1)	4468(1)	155(1)	1595(1)	41(1)
Si(1)	8209(2)	331(1)	1484(1)	50(1)
Si(2)	7952(2)	7(1)	3390(1)	56(1)
Si(3)	4557(2)	−289(1)	3696(1)	63(1)
O(1)	8326(4)	−54(3)	2484(2)	70(2)
O(2)	6198(4)	−1(3)	3619(2)	72(2)
C(1)	6204(5)	903(3)	1150(2)	42(2)
C(2)	5456(6)	819(3)	488(3)	50(2)
C(3)	3906(6)	1325(3)	459(3)	56(2)
C(4)	3638(6)	1732(3)	1100(3)	59(2)
C(5)	5045(5)	1484(3)	1516(3)	49(2)
C(6)	4277(5)	−686(3)	2831(2)	47(2)
C(7)	5418(6)	−1263(3)	2454(3)	50(2)
C(8)	4738(6)	−1394(3)	1805(3)	57(2)
C(9)	3193(7)	−906(4)	1772(3)	60(2)
C(10)	2885(6)	−468(4)	2396(3)	59(2)
C(11)	8961(6)	−820(4)	1175(4)	80(3)
C(12)	9353(6)	1320(4)	1001(3)	75(3)
C(13)	8273(8)	1227(5)	3395(4)	110(4)
C(14)	9187(8)	−1109(5)	4132(3)	113(4)
C(15)	4538(9)	−1392(5)	4682(3)	121(4)
C(16)	3068(7)	860(5)	3670(4)	108(4)
Fe(2)	3787(1)	5255(1)	1546(1)	42(1)
Si(4)	3142(2)	5666(1)	3403(1)	56(1)
Si(5)	−95(2)	5168(1)	3381(1)	59(1)
Si(6)	107(2)	4956(1)	1629(1)	54(1)
O(3)	1536(4)	5336(3)	3515(2)	82(2)
O(4)	−287(4)	5282(3)	2436(2)	68(2)
C(17)	3670(5)	6096(3)	2293(3)	48(2)
C(18)	5168(5)	5915(3)	1945(3)	53(2)
C(19)	5053(6)	6352(4)	1069(3)	58(2)
C(20)	3515(6)	6810(3)	850(3)	56(2)
C(21)	2662(5)	6660(3)	1596(3)	45(2)
C(22)	2181(5)	4453(3)	1573(3)	48(2)
C(23)	3225(6)	3894(3)	2255(3)	55(2)
C(24)	4716(6)	3700(3)	1948(3)	66(3)
C(25)	4632(7)	4105(4)	1072(4)	66(3)
C(26)	3095(6)	4567(4)	841(3)	59(3)
C(27)	4601(7)	4525(4)	4014(3)	100(3)
C(28)	2962(8)	6735(4)	3783(3)	94(3)
C(29)	−216(9)	3868(5)	4080(4)	131(4)
C(30)	−1590(8)	6162(6)	3578(4)	132(5)
C(31)	−551(6)	6130(4)	693(3)	83(3)
C(32)	−891(6)	3934(4)	1709(4)	86(3)

[a] Equivalent isotropic *U* defined as one-third of the trace of the orthogonalized $\mathbf{U}_{ij}$ tensor.

Homopolymerization Experiments. When the siloxane-bridged [n]ferrocenophanes **1a**, **1b**, **2**, and **3** were heated at 200 °C in the absence of added initiator, no increase in viscosity was noted, which suggested that ROP had not occurred. Analysis of the tube contents by ^{29}Si NMR showed that no new products had formed. The thermal stability of **1a**, **1b**, **2**, and **3** contrasts with the behavior of cyclic borasiloxanes, which undergo extensive ring–ring transformation reactions under these conditions.[5] In order to induce reactions, melt thermolyses were carried out in the presence of K[OSiMe$_3$], a well-known catalyst for the ROP of cyclic siloxanes.[3]

Using concentrations of the base initiator of 10 mol % at 200 °C, it was found that the siloxanylferrocenophanes **1a**, **2**, and **3** underwent extensive reactions to give new, mainly molecular products, of which most could be well-characterized by a combination of ^{29}Si NMR and mass spectrometry. For example, when **1a** was heated at 200 °C for 7 days in the presence of 10 mol % of K[OSiMe$_3$] again no significant increase in viscosity was observed, but analysis of the product mixture by ^{29}Si NMR indicated the presence of unreacted **1a** (35%) and also showed that ring-expansion reactions to yield the 1,3,5 trisila-2,4-dioxaferrocenophane **2** (10%) and the 1,3,5,7-tetrasila-2,4,6-trioxaferrocenophane **3** (10%) had occurred. In addition, the

Table 7. Selected Bond Lengths and Angles for **2** (Estimated Standard Deviations Given in Parentheses)

	Bond Lengths (Å)		
Fe(1)–C(1)	2.062(5)	Fe(1)–C(2)	2.051(4)
Fe(1)–C(3)	2.047(4)	Fe(1)–C(4)	2.040(4)
Fe(1)–C(5)	2.041(5)	Fe(1)–C(6)	2.051(4)
Fe(1)–C(7)	2.028(3)	Fe(1)–C(8)	2.051(5)
Fe(1)–C(9)	2.045(6)	Fe(1)–C(10)	2.053(5)
Si(1)–O(1)	1.617(3)	Si(1)–C(1)	1.836(4)
Si(1)–C(11)	1.871(6)	Si(1)–C(12)	1.866(6)
Si(2)–O(1)	1.623(4)	Si(2)–O(2)	1.615(4)
Si(2)–C(13)	1.834(8)	Si(2)–C(14)	1.797(5)
Si(3)–O(2)	1.623(4)	Si(3)–C(6)	1.845(5)
Si(3)–C(15)	1.844(5)	Si(3)–C(16)	1.835(7)
C(1)–C(2)	1.431(7)	C(1)–C(5)	1.439(6)
C(2)–C(3)	1.407(7)	C(3)–C(4)	1.417(8)
C(4)–C(5)	1.411(7)	C(6)–C(7)	1.437(6)
C(6)–C(10)	1.424(7)	C(7)–C(8)	1.415(8)
C(8)–C(9)	1.397(7)	C(9)–C(10)	1.422(8)
Fe(2)–C(17)	2.053(5)	Fe(2)–C(18)	2.032(6)
Fe(2)–C(19)	2.057(6)	Fe(2)–C(20)	2.048(4)
Fe(2)–C(21)	2.041(4)	Fe(2)–C(22)	2.049(5)
Fe(2)–C(23)	2.036(4)	Fe(2)–C(24)	2.027(4)
Fe(2)–C(25)	2.063(6)	Fe(2)–C(26)	2.040(7)
Si(4)–O(3)	1.615(4)	Si(4)–C(17)	1.858(5)
Si(4)–C(27)	1.834(5)	Si(4)–C(28)	1.844(7)
Si(5)–O(3)	1.601(5)	Si(5)–O(4)	1.606(4)
Si(5)–C(29)	1.820(7)	Si(5)–C(30)	1.821(8)
Si(6)–O(4)	1.627(4)	Si(6)–C(22)	1.851(5)
Si(6)–C(31)	1.845(4)	Si(6)–C(32)	1.855(7)
C(17)–C(18)	1.452(7)	C(17)–C(21)	1.418(6)
C(18)–C(19)	1.413(7)	C(29)–C(20)	1.398(7)
C(20)–C(21)	1.435(6)	C(22)–C(23)	1.419(6)
C(22)–C(26)	1.447(7)	C(23)–C(24)	1.420(7)
C(24)–C(25)	1.411(8)	C(25)–C(26)	1.402(7)
	Bond Angles (deg)		
Si(1)–O(1)–Si(2)	156.8(2)	O(3)–Si(5)–O(4)	109.4(2)
Si(2)–O(2)–Si(3)	160.7(3)	O(1)–Si(1)–C(1)	108.8(2)
Si(4)–O(3)–Si(5)	165.7(2)	O(2)–Si(3)–C(6)	109.4(2)
Si(5)–O(4)–Si(6)	155.4(2)	O(3)–Si(4)–C(17)	110.5(2)
O(1)–Si(2)–O(2)	111.4(2)	O(4)–Si(6)–C(22)	110.9(2)

formation of the cyclotetrasiloxane $[Me_2SiO]_4$ (9%) and higher cyclic siloxane oligomers $[Me_2SiO]_x$ ($\delta = -21.1$ to -21.8 ppm, $x = 5$–7) and $[Me_2SiO]_n$ ($\delta = -21.5$ ppm, 20%) was detected. Small peaks at ca. 0.4 ppm and around -21.5 ppm (ca. 16%) could not be conclusively assigned to any product. However, on the basis of evidence from a mass spectrum of the reaction products these peaks probably arise from ferrocenyl terminated linear siloxane oligomers of structure **4** (Scheme 2). Analysis by mass spectrometry provided evidence for all of the aforementioned products identified by ^{29}Si NMR including cyclic siloxanes up to $[Me_2SiO]_{15}$. In addition, peaks assigned to species of structure **4** were found at m/z (%) 724 (3 , M^+ for **4** ($x = 4$)), 650 (5, M^+ for **4** ($x = 3$)), and 576 (5, M^+ for **4** ($x = 2$)). Further evidence for the assignment of the ^{29}Si NMR resonances at ca. 0.4 and -21.5 ppm to compounds of structure **4** was provided by the determination of the ^{29}Si NMR spectrum of **4** ($x = 1$). This species was prepared via the previously reported method involving the hydrolysis of a silicon-bridged [1]ferrocenophane precursor[12b] and showed a single singlet ^{29}Si NMR resonance at 0.4 ppm. Significantly, this is at the same chemical shift as the low-field resonances assigned to species of type **4** in the ^{29}Si NMR spectrum of the reaction products.

The 1,3,5-trisila-2,4-dioxaferrocenophane **2** and the 1,3,5,7-tetrasila-2,4,6-trioxaferrocenophane **3** yielded a similar distribution of products when heated with $K[OSiMe_3]$ under the same conditions as **1a**, and again, no significant increase in viscosity was noted. Interestingly, in the case of **2**, traces of larger ring ferrocenophanes **5** ($x = 4$ or 5) were detected by mass spectrometry (Scheme 3). In contrast to the situation for **1a**, **2**, and **3**, analysis by ^{29}Si NMR and mass spectrometry identified no new products for the phenylated species **1b**. This species therefore also appears to be unreactive at elevated temperatures in the presence of $K[OSiMe_3]$.

Table 8. Final Fractional Atomic Coordinates and Equivalent Isotropic Displacement Coefficients (Å^2) for the Non-Hydrogen Atoms of **3** (Estimated Standard Deviations Given in Parentheses)

atom	x	y	z	U_{eq}[a]
Fe(1A)	0.1035(1)	0.7552(1)	0.2519(1)	0.052(1)
Si(1A)	0.0183(2)	0.6125(1)	0.1454(1)	0.052(1)
Si(2A)	0.0776(2)	0.6633(1)	0.0042(1)	0.057(1)
Si(3A)	0.0791(2)	0.8368(1)	0.0032(1)	0.056(1)
Si(4A)	0.1663(2)	0.8934(1)	0.1423(1)	0.058(1)
O(1A)	0.0558(5)	0.6531(3)	0.0804(3)	0.076(3)
O(2A)	0.0758(6)	0.7503(3)	−0.0134(3)	0.097(3)
O(3A)	0.1150(5)	0.8480(3)	0.0792(3)	0.076(3)
C(1A)	−0.0003(6)	0.6830(5)	0.2080(4)	0.047(3)
C(2A)	0.0105(6)	0.6730(5)	0.2783(4)	0.057(3)
C(3A)	−0.0121(7)	0.7390(6)	0.3106(4)	0.068(4)
C(4A)	−0.0366(6)	0.7931(5)	0.2619(5)	0.064(4)
C(5A)	−0.0298(5)	0.7591(5)	0.1993(4)	0.055(3)
C(6A)	0.1990(6)	0.8254(5)	0.2086(4)	0.053(3)
C(7A)	0.2277(6)	0.7501(5)	0.2008(5)	0.060(3)
C(8A)	0.2450(7)	0.7178(6)	0.2647(6)	0.079(5)
C(9A)	0.2297(7)	0.7728(7)	0.3114(5)	0.088(5)
C(10A)	0.2016(7)	0.8386(6)	0.2786(5)	0.070(4)
C(11A)	−0.1018(7)	0.5660(5)	0.1235(5)	0.079(4)
C(12A)	0.1108(7)	0.5444(5)	0.1766(5)	0.082(4)
C(13A)	−0.0184(7)	0.6169(5)	−0.0494(5)	0.089(4)
C(14A)	0.2001(7)	0.6251(7)	−0.0090(5)	0.111(6)
C(15A)	−0.0455(7)	0.8756(7)	−0.0125(6)	0.117(6)
C(16A)	0.1661(7)	0.8801(6)	−0.0497(5)	0.092(5)
C(17A)	0.0795(7)	0.9631(5)	0.1710(5)	0.083(4)
C(18A)	0.2785(7)	0.9408(6)	0.1172(5)	0.089(4)
Fe(1B)	0.4140(1)	0.2447(1)	−0.0040(1)	0.054(0)
Si(1B)	0.3337(2)	0.1063(1)	−0.1164(1)	0.055(1)
Si(2B)	0.4049(2)	0.1621(1)	−0.2529(1)	0.052(1)
Si(3B)	0.3985(2)	0.3356(2)	−0.2483(1)	0.059(1)
Si(4B)	0.4811(2)	0.3886(1)	−0.1065(1)	0.061(1)
O(1B)	0.3824(5)	0.1476(3)	−0.1776(3)	0.078(3)
O(2B)	0.4112(5)	0.2499(3)	−0.2664(3)	0.089(3)
O(3B)	0.4320(5)	0.3478(3)	−0.1716(3)	0.085(3)
C(1B)	0.3117(6)	0.1744(5)	−0.0519(4)	0.051(3)
C(2B)	0.3206(7)	0.1607(6)	0.0181(4)	0.062(4)
C(3B)	0.2960(7)	0.2262(7)	0.0514(5)	0.080(4)
C(4B)	0.2731(7)	0.2817(6)	0.0043(5)	0.078(4)
C(5B)	0.2826(5)	0.2504(5)	−0.0584(5)	0.062(3)
C(6B)	0.5115(6)	0.3176(5)	−0.0432(4)	0.055(3)
C(7B)	0.5400(6)	0.2425(5)	−0.0528(5)	0.062(4)
C(8B)	0.5553(7)	0.2073(6)	0.0094(6)	0.082(5)
C(9B)	0.5367(7)	0.2605(7)	0.0594(5)	0.086(5)
C(10B)	0.5101(7)	0.3270(6)	0.0271(5)	0.069(4)
C(11B)	0.2139(7)	0.0641(5)	−0.1466(5)	0.086(5)
C(12B)	0.4190(7)	0.0337(5)	−0.0820(5)	0.087(5)
C(13B)	0.3042(6)	0.1233(5)	−0.3092(4)	0.072(4)
C(14B)	0.5263(7)	0.1218(6)	−0.2674(5)	0.086(4)
C(15B)	0.2700(7)	0.3648(7)	−0.2627(5)	0.118(6)
C(16B)	0.4802(7)	0.3875(6)	−0.3002(5)	0.088(4)
C(17B)	0.3937(7)	0.4567(5)	−0.0761(5)	0.087(5)
C(18B)	0.5954(8)	0.4361(6)	−0.1276(5)	0.102(5)

[a] Equivalent isotropic U defined as one-third of the trace of the orthogonalized $\mathbf{U}_{ij}$ tensor.

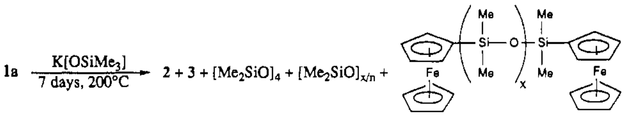
In order to investigate whether similar polymerization behavior would be detected for methylated siloxane-bridged ferrocenophanes in solution some additional experiments were carried out with compound **2**. When **2** was treated with 10 mol % of $K[OSiMe_3]$ in diethyl ether solution, much slower redistribution reactions were detected and the main products identified by ^{29}Si NMR and mass spectrometry (other than unreacted **2**) were oligomeric cyclic siloxanes. The reaction of **2** with triflic acid as a representative acid initiator was also explored in solution. When **2** was treated with 1 mol % of triflic acid in CH_2Cl_2 the main product by ^{29}Si NMR was found to be the polymer $[Me_2SiO]_n$. In addition, large quantities of ferrocene were identified by ^{1}H NMR.

Copolymerization Experiments. As no evidence for the ho-

Table 9. Selected Bond Lengths and Angles for **3** (Estimated Standard Deviations Given in Parentheses)

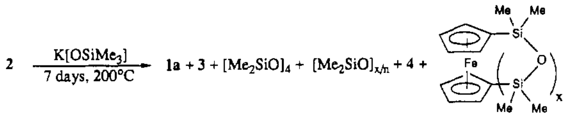
	Bond Lengths (Å)		
Fe(1A)–C(1A)	2.070(8)	Fe(1A)–C(2A)	2.041(9)
Fe(1A)–C(3A)	2.050(9)	Fe(1A)–C(4A)	2.037(9)
Fe(1A)–C(5A)	2.030(7)	Fe(1A)–C(6A)	2.048(9)
Fe(1A)–C(7A)	2.035(8)	Fe(1A)–C(8A)	2.028(9)
Fe(1A)–C(9A)	2.044(10)	Fe(1A)–C(10A)	2.053(10)
Si(1A)–O(1A)	1.619(6)	Si(1A)–C(1A)	1.825(8)
Si(1A)–C(11A)	1.853(9)	Si(1A)–C(12A)	1.834(9)
Si(2A)–O(1A)	1.604(6)	Si(2A)–O(2A)	1.607(6)
Si(2A)–C(13A)	1.835(10)	Si(2A)–C(14A)	1.831(11)
Si(3A)–O(2A)	1.596(7)	Si(3A)–O(3A)	1.596(6)
Si(3A)–C(15A)	1.831(11)	Si(3A)–C(16A)	1.821(10)
Si(4A)–O(3A)	1.630(6)	Si(4A)–C(6A)	1.851(9)
Si(4A)–C(17A)	1.841(10)	Si(4A)–C(18A)	1.844(10)
C(1A)–C(2A)	1.433(11)	C(1A)–C(5A)	1.438(12)
C(2A)–C(3A)	1.403(13)	C(3A)–C(4A)	1.409(13)
C(4A)–C(5A)	1.418(13)	C(6A)–C(7A)	1.424(12)
C(6A)–C(10A)	1.437(13)	C(7A)–C(8A)	1.424(15)
C(8A)–C(9A)	1.395(17)	C(9A)–C(10A)	1.401(16)
Fe(1B)–C(1B)	2.068(8)	Fe(1B)–C(2B)	2.042(10)
Fe(1B)–C(3B)	2.042(10)	Fe(1B)–C(4B)	2.036(10)
Fe(1B)–C(5B)	2.026(8)	Fe(1B)–C(6B)	2.060(9)
Fe(1B)–C(7B)	2.029(9)	Fe(1B)–C(8B)	2.028(9)
Fe(1B)–C(9B)	2.047(10)	Fe(1B)–C(10B)	2.043(10)
Si(1B)–O(1B)	1.625(7)	Si(1B)–C(1B)	1.832(9)
Si(1B)–C(11B)	1.854(10)	Si(1B)–C(12B)	1.849(10)
Si(2B)–O(1B)	1.598(6)	Si(2B)–O(2B)	1.609(7)
Si(2B)–C(13B)	1.852(9)	Si(2B)–C(14B)	1.838(10)
Si(3B)–O(2B)	1.599(7)	Si(3B)–O(3B)	1.605(6)
Si(3B)–C(15B)	1.821(11)	Si(3B)–C(16B)	1.835(10)
Si(4B)–O(3B)	1.613(7)	Si(4B)–C(6B)	1.838(9)
Si(4B)–C(17B)	1.840(10)	Si(4B)–C(18B)	1.843(11)
C(1B)–C(2B)	1.436(12)	C(1B)–C(5B)	1.429(13)
C(2B)–C(3B)	1.412(15)	C(3B)–C(4B)	1.402(15)
C(4B)–C(5B)	1.406(14)	C(6B)–C(7B)	1.425(13)
C(6B)–C(10B)	1.438(13)	C(7B)–C(8B)	1.412(15)
C(8B)–C(9B)	1.432(17)	C(9B)–C(10B)	1.401(16)
	Bond Angles (deg)		
Si(1)–O(1)–Si(2)	157.4(5)	O(2)–Si(3)–O(3)	109.3(5)
Si(2)–O(2)–Si(3)	154.7(3)	O(4)–Si(6)–O(5)	110.1(5)
Si(3)–O(3)–Si(4)	154.8(5)	O(5)–Si(7)–O(6)	108.9(5)
Si(5)–O(4)–Si(6)	156.6(6)	O(1)–Si(1)–C(1)	108.5(5)
Si(6)–O(5)–Si(7)	154.4(7)	O(3)–Si(4)–C(6)	107.8(5)
Si(7)–O(6)–Si(8)	157.9(6)	O(4)–Si(5)–C(21)	108.8(5)
O(1)–Si(2)–O(2)	108.7(5)	O(6)–Si(8)–C(26)	107.7(5)

Scheme 2



4

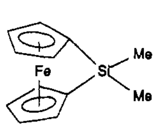
Scheme 3



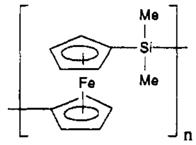
5 x > 3

mopolymerization of the siloxane-bridged [*n*]ferrocenophanes was detected under any of the conditions described above, attempts to copolymerize these species with other monomers were made. Specifically, the possible copolymerizations of **2** with the strained cyclotrisiloxane $[Me_2SiO]_3$ and the strained, ring-tilted [1]-ferrocenophane **6** were explored. Each of the latter monomers readily undergoes thermally induced ROP reactions to yield poly(dimethylsiloxane)[3] and the poly(ferrocenylsilane) **7**,[6] respectively.

When a 1:1 mixture of **2** and $[Me_2SiO]_3$ with 10 mol % of $K[OSiMe_3]$ was heated at 170°C for 23 h, no dramatic increase in viscosity was noted. The major products identified by ^{29}Si NMR were unreacted **2** (34%), poly(dimethylsiloxane) (36%), oligomeric siloxanes $[Me_2SiO]_x$ (8%), $[Me_2SiO]_4$ (7%), the ring-contraction product **1a** (7%), and the ring-expansion product **3** (6%). No evidence for the formation of high molecular weight poly(ferrocenylsiloxanes) was found. Similarly, when a 1:1 mixture of **2** and **6** was heated at 175 °C for 3.5 h, the major product besides unreacted **2** was the poly(ferrocenylsilane) **7**, which was formed via the independent ROP of **6**. Small amounts of **1a** were also detected. No evidence for the copolymerization of **2** and **6** was found.



6



7

Implications of the Results of the Polymerization Experiments. As was the case with cyclic borasiloxanes,[5] the siloxane-bridged [*n*]ferrocenophanes appear resistant to ROP reactions and instead yield an array of redistribution products under conditions where conventional cyclic siloxanes polymerize. The majority of the products formed presumably arise from siloxane bond cleavage and formation reactions which are promoted by the added base or acid initiator. However, the formation of ferrocene and/or linear oligomers of structure **4** indicates that cleavage of the cyclopentadienyl–silicon bond also occurs under the reaction conditions. This is particularly the case for the reaction of **2** promoted by triflic acid where the main products detected were poly(dimethylsiloxane), $[Me_2SiO]_n$, and ferrocene. Although close similarities clearly exist between the polymerization behavior of cyclic borasiloxanes and that of siloxane-bridged [*n*]ferrocenophanes, a significant difference was that the thermally induced redistribution reactions for the latter were much more sluggish and required significantly higher temperatures and larger quantities of initiator for reactions to occur to an appreciable extent.

Summary

A series of siloxane-bridged [*n*]ferrocenophanes of different ring-size has been synthesized and structurally characterized. The methylated siloxane-bridged [*n*]ferrocenophanes **1a**, **2**, and **3** were found to undergo redistribution reactions rather than ROP in the presence of base or acid initiators to yield, in varying quantities, other siloxane-bridged [*n*]ferrocenophanes together with cyclic siloxane oligomers and products derived from the cleavage of the cyclopentadienyl carbon–silicon bond such as ferrocene and the ferrocenyl-terminated siloxane oligomers **4**. In contrast, no analogous reactions were detected for the phenylated 1,3-disila-2-oxaferrocenophane **1b**. Presumably in the case of this species the presence of bulky phenyl side groups leads to significant kinetic and thermodynamic stabilization.

The polymerization behavior of siloxane-bridged [*n*]ferrocenophanes is reminiscent of that detected previously for cyclic borasiloxanes[5] and differs dramatically from that of most strained, ring-tilted [1]- and [2]metallocenophanes which generally undergo ROP.[6,7] Neither of the former two classes of compound function as precursors to poly(heterosiloxanes) via ROP as extrusion of ferrocene or boroxine units to yield siloxanes is thermodynamically favored. The design and synthesis of strained cyclic heterosiloxanes which are resistant to heterofragment extrusion therefore remains a challenge which must be overcome for the successful synthesis of poly(heterosiloxanes) via ring-opening methods. Further work toward this end is in progress.

Experimental Section

Materials. Halogenated siloxanes and tmeda were purchased from Huls and from Aldrich respectively and were distilled prior to use (the latter from CaH_2). Triflic acid (Aldrich), 1.6 M butylithium in hexanes

(Aldrich), ferrocene (Aldrich), and potassium trimethylsilanolate (Huls) were used as received. Dilithioferrocene–tetramethylenediamine was prepared via the reaction of ferrocene with BuLi in the presence of tmeda.[13] All reactions and manipulations were carried out under an atmosphere of prepurified nitrogen using either Schlenk techniques or an inert-atmosphere glovebox (Vacuum Atmospheres). Solvents were dried by standard methods, distilled, and stored under nitrogen over activated molecular sieves.

Equipment. The 200- or 400-MHz ^{1}H NMR spectra and 50.3- or 100.5-MHz ^{13}C NMR spectra were recorded either on a Varian Gemini 200 or a Varian XL 400 spectrometer. The 79.3-MHz ^{29}Si NMR spectra were referenced externally to $SiMe_4$ and were recorded on a Varian XL 400 spectrometer utilizing either a normal (proton coupled) or a DEPT pulse sequence (proton decoupled) with a $^2J_{Si-H}$ coupling of 6.7 Hz. Where product weights are not reported, yields have been estimated using ^{29}Si NMR integration. The latter values have been corrected to the nearest percent and therefore the total of the percentage yields for any reaction may be slightly more or slightly less than 100%. Mass spectra were obtained with the use of a VG 70–250S mass spectrometer operating in an electron impact (EI) mode. Elemental analyses were performed by Canadian Microanalytical Services, Delta, B.C., Canada. All the polymerization experiments were conducted at least twice to verify the results.

Synthesis of $Fe(\eta^5\text{-}C_5H_4)_2SiR_2(OSiR_2)$ (1a) R = Me and (1b) R = Ph. Synthesis of 1a. Compound **1a** has been previously prepared by Kumada[12a] and by Schaaf and co-workers[10b] via the acid-catalyzed alcoholysis of the ferrocenyldisilane $Fe(\eta^5\text{-}C_5H_4)_2(SiMe_2)_2$ and the hydrolysis of $Fe(\eta^5\text{-}C_5H_4SiMe_2OEt)_2$, respectively. We have used two alternative procedures to prepare this compound.

Procedure A. To a cooled (–78 °C) suspension of dilithioferrocene–tetramethylenediamine (5.0 g, 16 mmol) in dry ether (200 mL), distilled 1,3-dichlorotetramethyldisiloxane (3.1 mL, 3.2 g, 16 mmol) in 200 mL of the same solvent was added dropwise via a double tip syringe. The mixture was allowed to stir and was then filtered to remove the lithium chloride byproduct. Purification was achieved by chromatography on an alumina/hexane column. Elution with a 8:5 mixture of hexane–ether gave an orange-red band, which yielded the crystalline product. Yield: 0.9 g (18%). ^{29}Si NMR ($CDCl_3$): $\delta = 1.1$ ppm; (C_6D_6) $\delta = 0.9$ ppm. ^{1}H NMR ($CDCl_3$): $\delta = 4.35$ (m, 4H, Cp), 4.20 (m, 4H, Cp), 0.26 ppm (s, 12H, SiMe). ^{13}C NMR ($CDCl_3$) $\delta = 73.9$, 71.8 (s, (α and β Cp)), 71.3 (s, Cp C–Si), 1.6 ppm (s, SiMe). MS (EI, 70eV): m/z (%) = 316 (100, M^+), 301 (80, $M^+ - Me$), 285 (10, $M^+ - Me - MeH$), 186 (10, $Fe(\eta^5\text{-}C_5H_5)_2$).

Procedure B. To a solution of a 10-fold excess of dichlorodimethylsilane (23.0 mL, 0.19 mol) in 300 mL of hexane, a slurry of dilithioferrocene–tetramethylenediamine (6.1g, 19 mmol) in 70 mL of the same solvent was added dropwise. The reaction mixture was left to stir overnight and was filtered to remove lithium chloride. Solvent removal, and distillation of the residue yielded ca. 2.5 g of a dark red liquid (bp 80 °C (0.07 mmHg)) . The mixture was poured onto ice and extracted with ether, and the solvent was removed. Purification was achieved by chromatography on an alumina/hexane column. Elution with a 7:3 mixture of hexane–ether gave an orange-red band, which yielded the crystalline product. Yield: 0.75 g (13%).

Synthesis of 1b. To a cooled (–78 °C) suspension of dilithioferrocene–tetramethylenediamine (16.8 g, 53.0 mmol) in ether (400 mL) was added distilled 1.3-dichlorotetraphenyldisiloxane (12.2 g, 53.0 mmol) in 200 mL of the same solvent dropwise via a double tip syringe. The reaction mixture was allowed to stir overnight and was then filtered. After removal of the solvent under vacuum, the product was purified by recrystallization from hexanes. This yielded **1b** as pale yellow crystals. Yield: 2.3g (8%). ^{29}Si NMR ($CDCl_3$): –15.4 ppm. ^{1}H NMR ($CDCl_3$): $\delta = 7.73$ (m, 6H, Ph), 7.70 ppm (m, 6H, Ph), 7.36 (m, 8H, Ph), 4.35 (m, 4H, Cp), 4.21 ppm (m, 4H, Cp). MS (EI, 70 eV): m/z (%) = 564 (100, M^+), 486 (5, $M^+ - Ph$), 408 (3, $M^+ - Ph - PhH$).

Synthesis of $Fe(\eta^5\text{-}C_5H_4)_2(SiMe_2O)_2SiMe_2$ (2). To a cooled (–78 °C) suspension of dilithioferrocene–tetramethylenediamine (2.5 g, 7.9 mmol) in dry ether (300 mL), cooled (–78 °C) 1,5- dichlorohexamethyltrisiloxane (2.2 g, 7.9 mmol) in the same solvent (75 mL) was added dropwise. The orange-red mixture was allowed to warm to room temperature and to stir overnight. After filtration to remove lithium chloride, the solvent was removed under vacuum (0.01 mmHg). The desired compound was purified via two high vacuum distillations (45 °C, 0.05 mmHg) to remove ferrocene and other impurities. This yielded the bright orange-red crystalline product. Yield: 3.0 g (61%). ^{29}Si NMR: ($CDCl_3$) $\delta = -0.5$ (s, 2Si), –21.9 ppm (s, 1Si); (C_6D_6) $\delta = -0.1$ (s, 2Si), –22.1 ppm (s, 1Si). ^{1}H NMR ($CDCl_3$): $\delta = 4.35$ (m, 4H, Cp), 4.20 (m, 4H, Cp), 0.29 (s, 12H, SiMe), 0.20 ppm (s, 6H, Si–Me). ^{13}C NMR ($CDCl_3$) $\delta = 73.4$, 71.4 (s, (α and β Cp)), 70.6 (s, Cp C–Si), 2.3 (s, 4C, Si–Me), 1.7 ppm (s, 2C, Si–Me). MS (EI, 70 eV): m/z (%) = 390 (100, M^+), 375 (60, $M^+ - Me$), 316 (40, M^+ for **1**), 301 (45, M^+ for **1** – Me). Anal. Calcd for **2**: C, 49.22; H, 6.71. Found: C, 49.55; H, 6.55.

Synthesis of $Fe(\eta^5\text{-}C_5H_4)_2(SiMe_2O)_3SiMe_2$ (3). To a suspension of dilithioferrocene–tetramethylenediamine (5.0 g, 16 mmol) in 150 mL of dry ether at –78 °C was added 4.83 mL (16 mmol) of freshly distilled 1,7-dichlorooctamethyltetrasiloxane in 100 mL of ether dropwise via a double tip syringe. The mixture was stirred at –78 °C for 3 h and was then allowed to warm slowly to room temperature and allowed to stir overnight. Filtration (to remove lithium chloride), followed by solvent removal and purification by vacuum distillation (55 °C, 0.01 mmHg) yielded the bright orange-red crystalline product. Yield: 3.0 g (40%). ^{29}Si NMR: ($CDCl_3$) $\delta = 0.0$ (s, 2Si), –20.4 ppm (s, 2Si); (C_6D_6) $\delta = -0.5$ (s, 2Si), –20.9 ppm (s, 2Si). ^{1}H NMR ($CDCl_3$): $\delta = 4.48$ (m, 4H, Cp), 4.37 (m, 4H, Cp), 0.48 (s, 12H, Si–Me), 0.35 ppm (s, 12H, Si–Me). ^{13}C NMR ($CDCl_3$): $\delta = 73.5$, 72.4 (s, (α and β Cp)), 71.3 (s, Cp C–Si), 2.8 (s, 4C, Si–CH_3), 1.8 ppm (s, 4C, Si–CH_3). MS (EI, 70 eV): m/z (%) = 464 (100, M^+), 449 (8, $M^+ - Me$), 390 (2, M^+ for **2**), 375 (12, M^+ for **2** – Me), 316 (4, M^+ for **1**), 301 (12, M^+ for **1** – Me). Anal. Calcd for **3**: C, 46.53; H, 6.94. Found: C, 46.06; H, 6.64.

Synthesis of $Fc(SiMe_2O)_xSiMe_2Fc$ (4, $x = 1$) (Fc = $Fe(\eta^5\text{-}C_5H_4)(\eta^5\text{-}C_5H_5)$. This compound was prepared via a modification of the method mentioned briefly by Wrighton and co-workers.[12b]

To a solution of the silicon-bridged [1]ferrocenophane **7** (0.69 g, 3.0 mmol) in THF (15 mL) was added water dropwise (0.027 mL, 1.5 mmol). The reaction mixture was left to stir for 1 h, after which the solvent was removed. The residue was extracted with hexanes. Solvent removal from the extract yielded a reddish oily product, which was purified by column chromatography on alumina. Elution with a 1:4 mixture of dichloromethane–hexane produced a band which yielded the desired product as an orange-red crystalline material. Yield: 0.23 g (31%). The product was characterized by ^{29}Si and ^{1}H NMR and by mass spectrometry. ^{29}Si NMR (C_6D_6): $\delta = 0.4$ ppm. ^{1}H NMR (C_6D_6): $\delta = 4.21$ (m, 4H, $\eta^5\text{-}C_5H_4$)), 4.09 (m, 4H, $\eta^5\text{-}C_5H_4$)), 4.01 (s, 10H, $\eta^5\text{-}C_5H_5$), 0.40 ppm (s, 12H, Si–Me). MS (EI, 70 eV): m/z (%) = 502 (100, M^+ for **4** (x =1), 484 (3, $[Fe(\eta^5\text{-}C_5H_4)_2SiMe_2]_2$), 428 (15, $\{Fe(\eta^5\text{-}C_5H_4)(\eta^5\text{-}C_5H_4)\}_2SiMe_2$).

Polymerization Behavior of the Siloxane-Bridged [*n*]Ferrocenophanes 1a, 1b, 2, and 3. (a) Thermal Behavior of 1a, 1b, 2, and 3 in the Melt in the Absence of Added Initiator. Samples of the pure siloxane-bridged [*n*]ferrocenophanes (ca. 0.5 g) were heated in the melt at 200 °C in sealed evacuated Pyrex tubes for a period of 7 d. After this time analysis of the products by ^{29}Si NMR in $CDCl_3$ showed that no reaction had occurred.

(b) Reactions of 1a, 1b, 2, and 3 in the Melt Using $K[OSiMe_3]$ as Initiator. Samples of the pure siloxane-bridged [*n*]ferrocenophanes (ca. 0.5g) were mixed with 10 mol % of $K[OSiMe_3]$ in a sealed tube, and the mixture was heated in the melt at 200 °C for a period of 7 d. The products were extracted from the tube with a minimum amount of hexanes, and the solvent was removed under vacuum (>100 mmHg) and the products analyzed by ^{29}Si NMR (in $CDCl_3$) and mass spectrometry.

For **1a**, ^{29}NMR spectroscopy indicated that the products consisted of unreacted **1a** (35%), the siloxanylferrocenophanes **2** (10%) and **3** (10%), the cyclic siloxane $[Me_2SiO]_4$ ($\delta = -18.6$ ppm; 9%), higher cyclic siloxane oligomers $[Me_2SiO]_x$ ($x = 5$–7, $\delta = -21.1$ to –21.8) and $[Me_2SiO]_n$ ($\delta = -21.5$ ppm; ca. 20%). Small peaks at ca. 0.4 and ca. –21.5 ppm (ca. 16%) could not be conclusively assigned to any product, but on the basis of evidence from mass spectra these peaks probably arise from ferrocenyl terminated linear siloxane oligomers of structure **4**. Analysis by mass spectrometry provided evidence of all of the above species including cyclic siloxanes up to $[Me_2SiO]_{15}$. In particular peaks at m/z (%) 724 (3, M^+ for **4** ($x = 4$)), 650 (5, M^+ for **4** ($x = 3$)), and 576 (5, M^+ for **4** ($x = 2$)) provided evidence for the formation of linear species of type **4**.

When **1b** was heated under the same conditions with $K[OSiMe_3]$, no reaction was detected. Analysis by ^{29}Si NMR ($CDCl_3$) showed only a singlet resonance at $\delta = -15.4$ ppm assigned to **1b**, and a mass spectrum showed only peaks assigned to this species and logical fragmentation products. The same experimental procedures were used for **2** and **3** as for the 1,3-disila-2-oxaferrocenophanes **1a** and **1b** described above.

The reaction of **2** with 10 mol % of $K[OSiMe_3]$ in the melt for a period of 7 d led to the following identified by ^{29}Si NMR: unreacted **2** (6%), the siloxane-bridged [*n*]ferrocenophanes **1a** (62%) and **3** (4%), the cyclic siloxane $[Me_2SiO]_4$ (5%), higher cyclic siloxane oligomers $[Me_2SiO]_x$ (x

= 5–7) (6%), and the polymer $[Me_2SiO]_n$ (8%). Several small peaks at ca. 0.4 and –21.5 ppm (ca. 9%) could not be conclusively assigned. However, as in the case of **1a** described above, mass spectrometry suggested that these peaks probably arise from ferrocenyl-terminated siloxane oligomers of structure **4**. Analysis by mass spectrometry provided evidence of all of the above species. Peaks at *m/z* (%) 650 (3 , M^+ for **4** (x = 3)) and 502 (22 , M^+ for **4** (x = 1)) provided evidence for species of structure **4**. In addition peaks at *m/z* 612 (3, M^+ for **5** (x = 5)), 595 (8, M^+ for **5** (x = 5) – Me), and 538 (12, M^+ for **5** (x = 4)) provided evidence for the formation of species of structure **5**. A peak at *m/z* 186 was assigned to ferrocene (10, M^+).

When **3** was heated with $K[OSiMe_3]$ under the same conditions as for **2** the products identified by ^{29}Si NMR were unreacted **3** (11%), the siloxane-bridged ferrocenophanes **1a** (35%) and **2** (8%), the cyclic siloxane $[Me_2SiO]_4$ (6%), and higher cyclic siloxane oligomers $[Me_2SiO]_x$ (x > 4) (30%). Small peaks at ca. 0.4 and –21.5 ppm (ca. 10%) could not be conclusively assigned, but on the basis of evidence from mass spectra these probably arise from species of structure **4**. Analysis by mass spectrometry provided evidence or all of the above species. In particular peaks at *m/z* (%) 724 (15, M^+ for **4** (x = 4)), 650 (13, M^+ for **4** (x = 3)), 576 (25, M^+ for **4** (x = 2)), and 502 (20, M^+ for **4** (x = 1)) provided evidence for the formation of linear species of type **4**. A peak at *m/z* 186 was assigned to ferrocene (12, M^+). The 100% peak was at *m/z* 73 and was assigned to $[Me_2SiO - H]^+$.

(c) Reactions of 2 in Solution with K[OSiMe₃] as Initiator. The 1,3,5-trisila-2,4-dioxaferrocenophane **2** (0.87 g, 2.2 mmol) was reacted with 10 mol % of $K[OSiMe_3]$ in ether (100 mL) at –78 °C for 3 h, and the reaction mixture was then allowed to warm to 25 °C and to stir overnight. The yellow-orange mixture was filtered through a minifrit and the solvent removed under vacuum (>100 mmHg). The products were then characterized by ^{29}Si NMR (in $CDCl_3$) and by mass spectrometry.

A ^{29}Si NMR spectrum (in $CDCl_3$) identified the tube contents to be unreacted starting material **2** (95%) together with small quantities of cyclic siloxane oligomers $[Me_2SiO]_x$ (x > 5) (δ = –21.1 to –21.8 ppm, 5%). Mass spectrometry showed the presence of these species and also showed peaks at *m/z* (%) = 612 (1, M^+ for **5** (x = 5)), 538 (3, M^+ for **5** (x = 4)), and 464 (30, M^+ for **3**). The 100% peak was at *m/z* 390 (M^+ for **2**).

(d) Reaction of 2 in Solution with CF₃SO₂OH as Initiator. To a cooled (–78 °C) solution of the 1,3,5-trisila-2,4-dioxaferrocenophane **2** (0.72 g, 1.8 mmol) in dichloromethane (30 mL) was added a solution of of triflic acid (ca. 10 mol %) in CH_2Cl_2 (4 mL) via a double-tip syringe. After 3 h the orange-red reaction mixture was warmed to room temperature and allowed to stir overnight. The solution was then filtered and the solvent removed under vacuum (<100 mmHg). Analysis by ^{29}Si and ^{1}H NMR (in $CDCl_3$) and mass spectrometry was then carried out. Analysis by ^{29}Si NMR showed the presence of the cyclic siloxane $[Me_2SiO]_4$ (10%) and higher cyclic siloxane oligomers $[Me_2SiO]_x$ (x > 4) (2%), as well as the siloxane polymer $[Me_2SiO]_n$ (88%). ^{1}H NMR showed the presence of ferrocene (δ = 4.1 ppm, s, Cp), $[Me_2SiO]_n$, and $[Me_2SiO]_4$. Mass spectrometry indicated the presence of siloxane oligomers. MS (EI, 70 eV): *m/z* (%) = 296 (10, M^+ for $[Me_2SiO]_4$), 281 (35, M^+ for $[Me_2SiO]_4$ – Me), 265 (6, M^+ for $[Me_2SiO]_4$ – Me – MeH), 223 (32, M^+ for $[Me_2SiO]_4$ – Me – $SiMe_2$), 207 (100, M^+ for $[Me_2SiO]_3$ – Me).

(e) Attempted Copolymerization of 2 with [Me₂SiO]₃ in the Presence of K[OSiMe₃]. The cyclotrisiloxane $[Me_2SiO]_3$ (0.13 g, 0.6 mmol) and **2** (0.24 g, 0.5 mmol) were combined in a Pyrex tube with 10 mol % of $K[OSiMe_3]$ and the tube was sealed under vacuum at –196 °C. The mixture was then heated at 170 °C for 23 h. No increase in viscosity was noted. The tube was then opened, and the products were then dissolved in THF and the resulting solution filtered. After solvent removal (at >100 mmHg) the products were analyzed by ^{29}Si NMR and by mass spectrometry. ^{29}Si NMR (C_6D_6): δ = –0.1, –22.1 (unreacted **2**, 34%), –21.6 ppm ($[Me_2SiO]_n$, 36%), 0.9 (**1a**, 7%), 0.5, –20.9 (**3**, 6%), –18.7 ($[Me_2SiO]_4$, 7%), –21.0 to –21.9 ($[Me_2SiO]_x$, x > 4, 8%), –1.2 ppm (unidentified, 2%). MS (EI, 70 eV): *m/z* (%) = 686 (3, M^+ for **5** (x = 6) , 612 (5, M^+ for **5** (x = 5)), 538 (5 , M^+ for **5** (x = 4)), 502 (3, M^+ for **4** (x = 1)), 464 (15, M^+ for **3**), 390 (100, M^+ for **2**), 375 (50, M^+ for **2** – Me), 316 (35, M^+ for **1a**), 301 (35, M^+ for **1a** – Me).

(f) Attempted Copolymerization of 2 with the [1]Ferrocenophane Fe(η^5-C₅H₄)₂SiMe₂ (6). The attempted copolymerization of **2** (0.30 g, 0.77 mmol) with the [1]ferrocenophane **6** (0.19 g, 0.77 mmol) was carried at 175 °C for 3.5 h in the absence of any added initiator. The resulting products were analyzed and characterized by ^{29}Si NMR and mass spectrometry. ^{29}Si NMR (C_6D_6): δ = –0.1, –22.0 (unreacted **2**, 60%), –6.4 (**7**, 27%), 0.9 ppm (**1a**, 13%). MS (EI, 70 eV): *m/z* (%) = 1210 (5, M^+ for $[Fe(\eta^5\text{-}C_5H_4)_2SiMe_2]_5$), 968 (5, M^+ for $[Fe(\eta^5\text{-}C_5H_4)_2SiMe_2]_4$), 726 (15, M^+ for $[Fe(\eta^5\text{-}C_5H_4)_2SiMe_2]_3$), 650 (10, M^+ for **4** (x = 3), 484 (100, M^+ for $[Fe(\eta^5\text{-}C_5H_4)_2SiMe_2]_2$), 390 (80, M^+ for **2**), 301 (15, M^+ for **1a** – Me), 243 (25, M^+ for **5** + H), 186 (20, M^+ for ferrocene).

X-ray Structure Determination Technique. Intensity data for the compounds were collected on an Enraf-Nonius CAD-4 diffractometer at room temperature, using graphite-monochromated Mo Kα radiation (λ = 0.71073 Å). The ω–2θ technique was applied with variable scan speeds. For each structure, the intensities of three standard reflections were measured every 2 h, and corrections were applied when necessary. The data were corrected for Lorentz and polarization effects, and empirical absorption corrections[16] were applied to each data set. The structures were solved by either Patterson or direct methods. Non-hydrogen atoms were refined anisotropically by full-matrix least-squares methods to minimize $\Sigma w(F_0 - F_c)^2$, where $w^{-1} = \sigma^2(F) + g(F)^2$. Hydrogen atoms were positioned on geometric grounds (C–H 0.96 Å) and included in the calculations (as riding atoms). Crystal data, data collection, and least-squares parameters are listed in Table 1. All calculations were performed and graphics created using SHELXTL PC[17] on a IBM 486-66 personal computer.

Acknowledgment. We thank the Natural Science and Engineering Research Council of Canada (NSERC) and the Ontario Center of Materials Research (OCMR) for financial support. We also thank the NSERC for a Scholarship (to D.B.Z.) and the University of Toronto for Open Fellowships (to C.A. and D.A.F.). We also thank Mr. Nick Plavac for obtaining the ^{29}Si NMR spectra.

Supplementary Material Available: Tables giving a summary of the crystal data and intensity collection parameters, atomic coordinates, complete bond lengths and angles, anisotropic thermal parameters, hydrogen atomic coordinates, and least-squares plane data and figures showing the molecular structures of **1a**, **1b**, **2**, and **3** (47 pages). Ordering information is given on any current masthead page.

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