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The Polymerization Behavior of [1]- and [2]Ferrocenophanes Containing Silicon Atoms in the Bridge: Comparison of the Molecular Structure of the Strained, Polymerizable Cyclic Ferrocenylsilane $Fe(\eta\text{-}C_5H_4)_2(SiMe_2)$ with That of the Cyclic Ferrocenyldisilane $Fe(\eta\text{-}C_5H_4)_2(SiMe_2)_2$

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The strained cyclic ferrocenylsilane $Fe(\eta\text{-}C_5H_4)_2(SiMe_2)$ (1), containing a single silicon atom in the bridge, undergoes thermal ring-opening polymerization at 130 °C to yield the high-molecular-weight poly(ferrocenylsilane) $[Fe(\eta\text{-}C_5H_4)_2(SiMe_2)]_n$ (2). In contrast, the analogous cyclic ferrocenyldisilane $Fe(\eta\text{-}C_5H_4)_2(SiMe_2)_2$ (3), with two silicon atoms in the bridge structure, is resistant to polymerization under the same conditions. In order to probe the reasons for the dramatic difference in polymerization behavior between 1 and 3, the molecular structures of these species have been determined by single-crystal X-ray diffraction. This has allowed the first structural comparison of [1]- and [2]ferrocenophanes with the same bridging atoms (silicon) and substituents (methyl). The cyclic ferrocenylsilane 1 was found to possess a strained, ring-tilted structure with an angle between the planes of the cyclopentadienyl rings of 20.8(5)°. In addition, considerable distortion from planarity was detected for the cyclopentadienyl carbon atom bonded to the bridging silicon moiety. In contrast, the cyclic ferrocenyldisilane 3 possesses a much less distorted structure and the corresponding tilt angle between the cyclopentadienyl ligands is only 4.19(2)°. Crystals of 1 are monoclinic, space group $P2_1/a$, with a = 7.438(3) Å, b = 10.322(4) Å, c = 15.575(6) Å, β = 99.04(3)°, V = 1180.9(8) Å^3, and Z = 4. Crystals of 3 are monoclinic, space group $P2_1/n$, with a = 10.433(2) Å, b = 8.703(1) Å, c = 17.243(2) Å, β = 107.32(1)°, V = 1494.6(12) Å^3, and Z = 4.

Introduction

Ring-opening polymerization is a well-established route to organic polymers and an increasingly successful method for the synthesis of polymers with main chains comprising inorganic elements.[1-4] In contrast, ring-opening routes to organometallic polymers are much less developed. Thus, apart from the cases of several cyclic organosilicon compounds such as silacycloolefins, silacycloalkynes, and silacyclobutanes, very few attempts to investigate this approach have been described.[5-7]

As part of our program to explore the synthesis and properties of new classes of inorganic[4] and organometallic[8] polymers, we recently reported[8a] the thermal ring-opening polymerization of the cyclic ferrocenylsilane 1 to yield the high-molecular-weight poly(ferrocenylsilane) 2.[8-10] In addition, we carried out measurements of the enthalpy of polymerization using differential scanning

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(6) Rauchfuss and Brandt have recently reported the synthesis of polyferrocenylene persulfides via the reaction of trithiaferrocenophanes with PBu_3. See: Brandt, P. F.; Rauchfuss, T. B. *J. Am. Chem. Soc.* **1992**, *114*, 1926.

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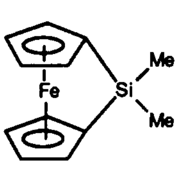

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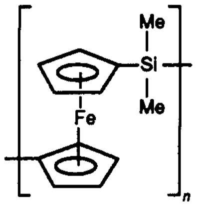

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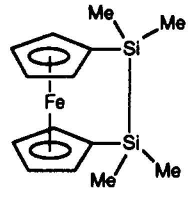

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calorimetry (DSC), which indicated the ring strain present in 1 to be ca 80 kJ mol^{-1}.[8a] Concurrent with this work, we have explored the polymerization behavior of the related cyclic ferrocenyldisilane 3, which contains an additional silicon atom in the bridge structure. In this paper we give full details of the thermal polymerization of 1 and, in addition, we describe our investigations of the polymerization behavior of 3 and provide a detailed comparison of the structures of 1 and 3 as determined by single-crystal X-ray diffraction.

Results and Discussion

Synthesis and Ring-Opening Polymerization of the Cyclic Ferrocenylsilane 1. The first reported [1]-ferrocenophane containing a single silicon atom in the bridge was the species $Fe(\eta\text{-}C_5H_4)_2(SiPh_2)$ (4), which was synthesized by Osborne and co-workers in 1975 via the reaction of dilithioferrocene·TMEDA (TMEDA = tetramethylethylenediamine) with diphenyldichlorosilane.[11] A subsequent X-ray crystal structure determination of 4 showed that the cyclopentadienyl ligands were significantly tilted with respect to one another by an angle of 19.1(10)°, which suggested that the compound was appreciably strained.[12] This is in contrast with the situation in ferrocene, in which the cyclopentadienyl ligands are parallel.[13] Subsequently, several species analogous to 4 have been prepared, including the methylated compound 1.[14,15] Further evidence for the presence of appreciable strain in these compounds was provided by the detection of facile, stoichiometric ring-opening reactions.[14,16] As the presence of ring strain is usually a prerequisite for ring-opening polymerization, we investigated the polymerization behavior of 1.[17]

The cyclic ferrocenylsilane 1 was prepared in ca. 60% yield as an orange-red, moisture-sensitive, crystalline material via the previously reported procedure involving the reaction of dilithioferrocene·TMEDA with dimethyldichlorosilane.[14] The identity of 1 was confirmed by ^{1}H NMR, mass spectrometry, and the melting point, which afforded data consistent with those reported in the literature.[14] We also determined the ^{13}C and ^{29}Si NMR spectra of 1 as these had not been previously reported.

Our initial attempts to polymerize 1 involved heating this species in the melt at elevated temperatures, and this procedure proved to be successful. Thus, when 1 was heated in an evacuated, sealed Pyrex tube at 130 °C, the tube contents became molten and then rapidly more viscous. After 10 min the tube contents were completely immobile and heating was then continued for a further 50 min at the same temperature. The polymeric product dissolved slowly but completely in THF, which indicated that no appreciable cross-linking had taken place. The poly(ferrocenylsilane) 2 was isolated as a yellow, fibrous material by repeated precipitation from THF first into hexanes and then into acetone. The yield of 2 was virtually quantitative, and unreacted 1 was not detected. Polymer 2 was structurally characterized by ^{1}H, ^{13}C, and ^{29}Si NMR spectroscopy and elemental analysis, and the molecular weight distribution was analysed by gel permeation chromatography (GPC). The ^{1}H NMR spectrum of 2 (in C_6D_6) showed two broad resonances for the cyclopentadienyl protons at 4.25 and 4.10 ppm and a broad resonance at 0.53 ppm assigned to the methyl groups attached to silicon. The ratio of these resonances was 4:4:6, as expected. The ^{13}C NMR spectrum of 2 (in C_6D_6) was also consistent with the assigned structure. Significantly, the unusual, high-field resonance at 33.5 ppm for the cyclopentadienyl carbon attached to silicon in the monomer 1 shifted to a more conventional value of 71.9 ppm in the ^{13}C NMR spectrum of the polymer 2. The ^{29}Si NMR spectrum of 2 consisted of a single, singlet resonance at -6.4 ppm, which is slightly shifted to high field compared to the monomer 1 (δ -4.6 ppm). Elemental analysis data for 2 were also consistent with the assigned structure. GPC indicated that 2 possessed an approximate weight-average molecular weight (M_w) of 5.2×10^5 and a number-average molecular weight (M_n) of 3.4×10^5 using polystyrene standards for column calibration. The molecular weight distribution was quite narrow, with a polydispersity of 1.5. Polymer 2 appears indefinitely stable to the atmosphere, and amber, free-standing films can be cast from solutions of the material in toluene via solvent evaporation.[17]

Synthesis and Polymerization Behavior of the Cyclic Ferrocenyldisilane 3. The facile thermal ring-opening polymerization of 1 suggested that related species containing more than one silicon atom in the bridge (such as 3) might also polymerize. The cyclic ferrocenyldisilane 3 was prepared in high yield as an orange, sublimable crystalline material by a modification[8b] of the previously reported method,[18] which involved the reaction of dilithioferrocene·TMEDA with the dichlorodisilane $ClMe_2Si{-}SiMe_2Cl$. The latter was prepared in two high-yield

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[9] After the paper listed as ref 8a was received by *J. Am. Chem. Soc.*, Pannell and co-workers made an independent report of the polymerization of 1 at the XXV Silicon Symposium, Los Angeles, CA, April 3–4, 1992: Pannell, K., private communication.

[10] Low-molecular-weight (1400–7000), partially characterized poly(ferrocenylsilanes) have previously been prepared via a polycondensation reaction involving dilithioferrocene and dialkyl and diaryldichlorosilanes: Rosenberg, H. U.S. Patent 3,426,053, 1969. In addition, Pannell and co-workers have reported the synthesis and characterization of polysilanes with ferrocenyl side groups. See: *Silicon-Based Polymer Science*; Zeigler, J. M., Fearon, F. W. G., Eds.; Advances in Chemistry 224; American Chemical Society: Washington DC, 1990; p 329.

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[15] Butler, I. R.; Cullen, W. R.; Rettig, S. J. *Can. J. Chem.* **1987**, *65*, 1452.

[16] The stoichiometric ring-opening reactions of 1 and related species have been used to derivatize surfaces. See, for example: Fischer, A. B.; Bruce, J. A.; McKay, D. R.; Maciel, G. E.; Wrighton, M. S. *Inorg. Chem.* **1982**, *21*, 1766.

[17] The ring-opening polymerization of cyclic ferrocenylsilanes such as 1 with different substituents attached to silicon appears to be quite general; for example, compound 4 also polymerizes. In addition, related species with atoms of other elements in the bridge such as phosphorus and germanium have also been found to polymerize.[8a,c,d] It should also be noted that Seyferth and co-workers have synthesized polymers of formula $[Fe(\eta\text{-}C_5H_4)_2(PPh)]_n$ via condensation routes; see: Withers, H. P.; Seyferth, D.; Fellmann, J. D.; Garrou, P.; Martin, S. *Organometallics* **1982**, *1*, 1283.

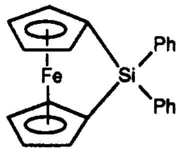
[18] Kumada, M.; Kondo, T.; Mimura, K.; Ishikawa, M. *J. Organomet. Chem.* **1972**, *43*, 293.

steps from Me_3SiCl.[19,20] The identity of 3 was confirmed by ^1H NMR, mass spectrometry, and a melting point determination, which afforded data consistent with those reported by Kumada,[18] and by ^{13}C and ^{29}Si NMR.[8b]

Compared to the situation in the cyclic ferrocenylsilane 1, the presence of an additional silicon atom in the bridge would be expected to reduce the ring strain present. Nevertheless, the presence of significant strain in 3 has been proposed to explain the ease with which this species undergoes acid-catalyzed alcoholysis of the Si–Si bond.[21] In addition, we have found that the cyclic ferrocenyldisilane 3 undergoes facile palladium-catalyzed insertions of alkynes and dienes into the Si–Si bond to yield larger rings and macrocycles.[8b] However, these insertion reactions are not necessarily indicative of the presence of significant ring strain, as alkynes are also known to insert into the Si–Si bonds of linear disilanes in the presence of transition-metal catalysts.[22] Significantly, spectroscopic data for 3 suggest that this species is not very strained. Thus, the ^{13}C NMR resonance for the cyclopentadienyl carbon atom bonded to silicon in 3 (in $CDCl_3$) occurs at 72.4 ppm, which is at a chemical shift similar to that for the complex $Fe(\eta\text{-}C_5H_4SiPh_3)_2$ (66.4 ppm in $CDCl_3$), where the bridge between the cyclopentadienyl ligands is absent.[23] This is in contrast with the situation in previously characterized strained [1]ferrocenophanes with group 14 (or group 15) elements in the bridge, where this resonance is shifted 35–60 ppm upfield compared to analogous compounds with nonbridged structures.[23] For example, for 1 the ^{13}C NMR resonance for the cyclopentadienyl carbon bonded to silicon appears at 33.5 ppm. The conventional ^{13}C NMR shift for 3 compared to that for 1 and related species indicates that little structural distortion is present at the carbon atom bonded to silicon. This suggests that the ring strain present in 3 is significantly less than that in 1. Further evidence for a relatively unstrained structure for 3 was provided by UV/visible spectroscopy. The UV/visible spectrum of 3 (in hexanes) in the region 300–600 nm showed two absorptions at 324 nm ($\epsilon = 62$ M^{-1} cm^{-1}) and at 444 nm ($\epsilon = 88$) and is very similar to that for ferrocene, which shows two bands at 324 nm ($\epsilon = 50$) and at 440 nm ($\epsilon = 90$). In contrast, in ferrocenophanes which possess significant ring tilting the higher wavelength band experiences a bathochromic shift and increases in intensity.[23] For example, the UV/visible spectrum of the crystallographically characterized ring-tilted cyclic ferrocenylsilane 4 in cyclohexane shows two bands at 322 nm ($\epsilon = 630$) and at 480 nm ($\epsilon = 270$).[14] Similarly, Wrighton and co-workers have reported the UV/visible spectrum of 1[14] and the longer wavelength band in hexane occurs at 478 nm ($\epsilon = 240$), which is also significantly shifted from that of ferrocene. These data are consistent with a strained, ring-tilted structure for 1 and a significantly less distorted structure for 3.

Attempts to thermally polymerize 3 involved heating this species in the melt in a manner analogous to that used to successfully polymerize 1. However, when 3 was heated in an evacuated tube at temperatures from 150 to 340 °C for several days, no increase in viscosity was detected and analysis of the tube contents by ^1H NMR showed only the presence of unreacted 3. In addition, analysis by GPC showed that no high-molecular-weight material ($M_w > 1000$) was present. As the thermal polymerization of 3 was unsuccessful, bearing in mind the recently reported anionic ring-opening polymerization of cyclic tetrasilanes to yield polysilanes,[2b] we also attempted to induce the polymerization of the cyclic ferrocenyldisilane 3 by using anionic initiators. However, when 3 was heated in the melt in the presence of a small quantity of $K[OSiMe_3]$ at 140–200 °C, no polymerization was detected. Similarly, attempts to induce the ring-opening polymerization of 3 in solution via the addition of small quantities of $K[OSiMe_3]$ or BuLi to 3 in THF were also unsuccessful. In all cases only unreacted 3 was isolated according to ^1H NMR analysis and GPC showed no evidence for the presence of high-molecular-weight material ($M_w > 1000$).

Because of the contrasting polymerization behavior of 1 and 3 the molecular structure of each of these species was determined by single-crystal X-ray diffraction. Two [1]ferrocenophanes containing silicon in the bridge have been previously characterized by X-ray crystallography, compound 4 and the halogenated species $Fe(\eta\text{-}C_5H_4)(\eta\text{-}C_5H_3R)(SiCl_2)$ ($R = CHMeNMe_3$; 5).[12,15] In addition, the structures of such species have been compared with those of [1]ferrocenophanes containing other bridging atoms such as germanium, phosphorus, arsenic, and zirconium.[24] The X-ray structures of several [2]ferrocenophanes such as the dicarbon-bridged species 6[25] have also been determined. However, to our knowledge no comparison of a [1]ferrocenophane with the related [2]ferrocenophane having the same bridging atoms and substituents has been reported. In view of this, our discussion of the structures of 1 and 3 focuses in particular on a direct comparison of the molecular features of these two species.



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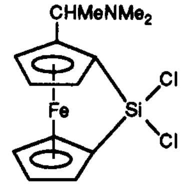

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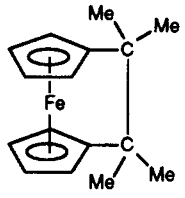

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Discussion and Comparison of the X-ray Structures of 1 and 3. Red-orange single crystals of 1 suitable for an X-ray diffraction study were obtained from a solution of the compound in hexanes at −50 °C over 12 h. Single crystals of 3 were obtained as diamond-shaped platelets by allowing a solution of the compound in hot hexanes to cool to room temperature. Two alternative views of the molecular structures of 1 and 3 are shown in parts a and b of Figures 1 and 2, respectively. A summary of cell constants and data collection parameters is included in Table I, and the fractional coordinates and important bond lengths and angles listed in Tables II and

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(20) Wilson, G. R.; Smith, A. G. *J. Org. Chem.* **1961**, *26*, 557.

(21) Kumada, M.; Kondo, T.; Mimura, K.; Yamamoto, K.; Ishikawa, M. *J. Organomet. Chem.* **1972**, *43*, 307. See p 312 for suggestion of ring strain.

(22) See, for example: Matsumoto, H.; Shono, K.; Wada, A.; Matsubara, I.; Watanabe, H.; Nagai, Y. *J. Organomet. Chem.* **1980**, *199*, 185 and references therein.

(23) Osborne, A. G.; Whiteley, R. H.; Meads, R. E. *J. Organomet. Chem.* **1980**, *193*, 345.

(24) (a) Seyferth, D.; Withers, H. P. *Organometallics* **1982**, *1*, 1275. (b) Broussier, R.; Da Rold, A.; Gautheron, B.; Dromzee, Y.; Jeannin, Y. *Inorg. Chem.* **1990**, *29*, 1817. (c) Butler, I. R.; Cullen, W. R.; Einstein, F. W. B.; Rettig, S. J.; Willis, A. J. *Organometallics* **1983**, *2*, 128. (d) Stoeckli-Evans, H.; Osborne, A. G.; Whiteley, R. H. *J. Organomet. Chem.* **1980**, *194*, 91.

(25) Burke Laing, M.; Trueblood, K. N. *Acta Crystallogr.* **1965**, *19*, 373.

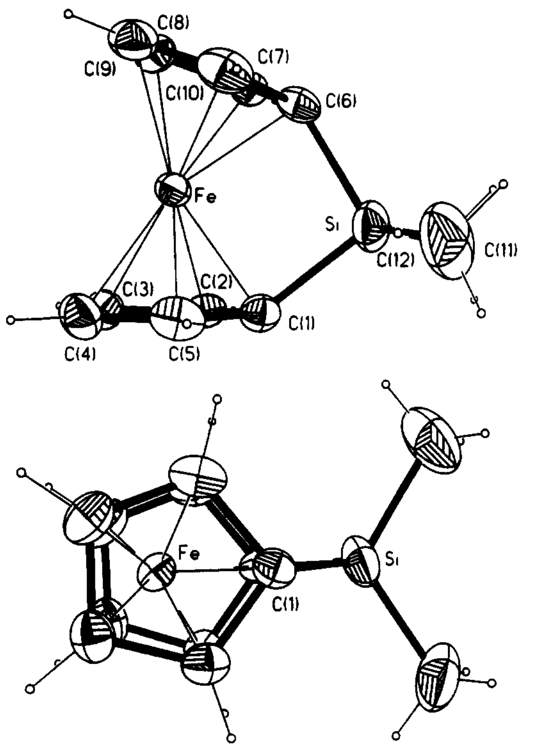

Figure 1. (a, top) Molecular structure of 1 (with thermal ellipsoids drawn at the 25% probability level). (b, bottom) Alternative view of a molecule of 1 (with thermal ellipsoids drawn at the 25% probability level).

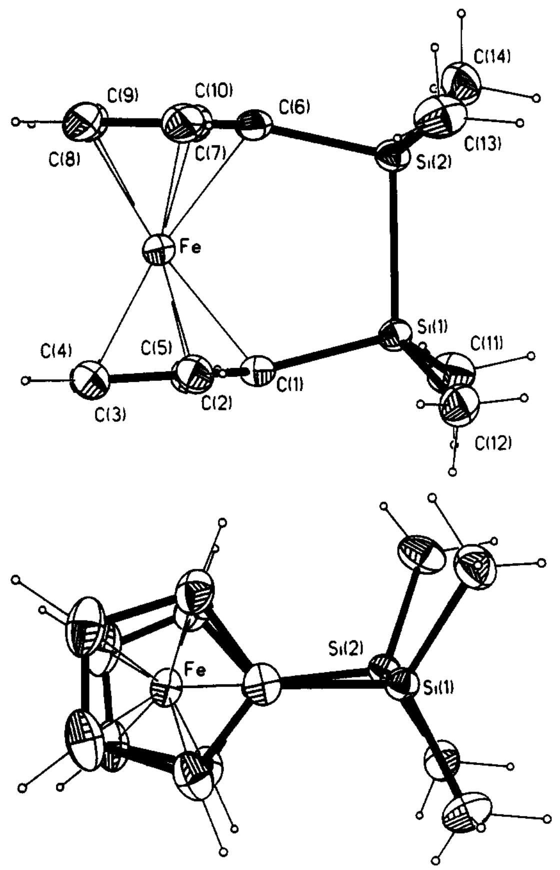

Figure 2. (a, top) Molecular structure of 3 (with thermal ellipsoids drawn at the 25% probability level). (b, bottom) Alternative view of a molecule of 3 (with thermal ellipsoids drawn at the 25% probability level).

Table I. Summary of Crystal Data and Intensity Collection Parameters

	1	3
empirical formula	$C_{12}H_{14}FeSi$	$C_{14}H_{20}FeSi_2$
M_r	242.2	300.4
cryst class	monoclinic	monoclinic
space group	$P2_1/a$	$P2_1/n$
a, Å	7.438(3)	10.433(2)
b, Å	10.322(4)	8.703(1)
c, Å	15.575(6)	17.243(2)
β, deg	99.04(3)	107.32(1)
V, Å^3	1180.9(8)	1494.6(12)
Z	4	4
D_{calc}, g cm^{-3}	1.36	1.34
μ(Mo Kα), cm^{-1}	13.4	11.4
F(000)	504	632
ω-scan width, deg	1.0 + 0.35 tan θ	0.7 + 0.35 tan θ
range θ collected, deg	1–22.5 ($\pm h,k,l$)	1–25 ($\pm h,k,l$)
total no. of rflns	1551	2900
no. of unique rflns	1507	2622
R_{int}	0.058	0.020
no. of obsd data used [$I > 3\sigma(I)$]	819	2131
weighting g	0.0004	0.0007
R	0.052	0.029
R_w	0.058	0.033
GOF	1.87	1.29
$(\Delta/\sigma)_{max}$ in last cycle	0.001	0.020
no. of params refined	127	235
$\Delta\rho$ in final ΔF map, e Å^{-3}	0.33	0.31

III for 1 and Tables IV and V for 3. The angles α, β, δ, and θ used in discussing the structures are defined in Figure 3.[23] The values of these angles for the compounds 1 and 3–6 are compiled in Table VI.

The most dramatic structural difference between 1 and 3 is the tilt angle α between the planes of the cyclopentadienyl rings (see Figures 1a and 2a). The value is 20.8(5)° in 1, whereas in 3 the value is much smaller (4.19(2)°). Indeed, the tilt angle in 3 is only slightly greater than that present in Fe(η-$C_5H_4SiMe_2SiMe_3$)$_2$ (α = 1.0(24)°), where the bridge between the cyclopentadienyl groups is absent.[26] The different degrees of ring tilting in 1 and 3 can also be appreciated by comparing the Cp–Fe–Cp angle δ. Thus, the value for δ in 1 (164.74(8)°) is indicative of greater tilting than that in 3 (176.48(3)°). Similarly, the displacement of the iron atom from the line joining the two centroids of the cyclopentadienyl ligands is significantly greater in 1 (0.2164(11) Å) compared to 3 (0.027(3) Å). Further evidence for the presence of additional strain in 1 is provided by the angle β between the plane of the cyclopentadienyl ligands and the C(Cp)–Si bonds. This angle has a much greater value in 1 (37.0(6)°) compared to 3 (10.8(3)°), and this dramatic distortion from planarity at the cyclopentadienyl carbon bonded to silicon is almost certainly the reason for the unusual high-field ^{13}C NMR resonance associated with this carbon atom in the former compound. The C(Cp)–Si–C(Cp) angle θ in 1 (95.7(4)°) is very small compared to an idealized value for sp^3-hybridized silicon of 109.5°. The small θ angle leads to a scissoring effect, which causes a widening of the C(Me)–Si–C(Me) angle to a value of 114.8(6)°. This is significantly greater than the corresponding value found in 3 (average 110.10(19)°). Interestingly, the bonds between the cyclopentadienyl carbon atoms and silicon differ very slightly between 1 and 3. Thus, in 1 the C(Cp)–Si bonds have an average length of 1.858(9)°, whereas in 3 the corresponding average length is 1.8765(26)°. The average lengths of the Si–C(Me) bonds, on the other hand (1.847(13) Å in 1 and 1.863(4) Å in 3) are identical within experimental error.

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Table II. Final Fractional Coordinates and Thermal Parameters for the Non-Hydrogen Atoms of 1

atom	x	y	z	U_{eq},[a] Å^2
Fe	0.18965(13)	0.99723(14)	0.16117(7)	4.64(7)
Si	0.2334(4)	1.0132(3)	0.33557(17)	7.48(19)
C1	0.0746(11)	1.0943(8)	0.2487(6)	5.1(5)
C2	−0.0584(10)	1.0230(8)	0.1917(7)	5.7(6)
C3	−0.0647(12)	1.0587(10)	0.1042(6)	6.4(7)
C4	0.0594(14)	1.1598(10)	0.1034(7)	7.3(8)
C5	0.1446(12)	1.1828(9)	0.1891(8)	6.8(7)
C6	0.3517(11)	0.9148(8)	0.2609(6)	5.3(6)
C7	0.2528(11)	0.8167(8)	0.2076(7)	5.5(6)
C8	0.2940(13)	0.8272(10)	0.1229(7)	7.0(7)
C9	0.4203(14)	0.9268(12)	0.1199(8)	8.4(8)
C10	0.4585(11)	0.9801(11)	0.2039(8)	7.4(7)
C11	0.3878(19)	1.1287(14)	0.3988(9)	13.3(12)
C12	0.1100(19)	0.9038(13)	0.4016(8)	13.3(12)

[a] $U_{eq} = (U_{11} + U_{22} + U_{33})/3$.

Table III. Selected Bond Lengths (Å) and Angles (deg) for 1 (Estimated Standard Deviations Are in Parentheses)

	Distances		
Fe–Si	2.690(3)	Si–C11	1.832(13)
Fe–C1	1.990(8)	Si–C12	1.862(12)
Fe–C2	1.994(7)	C1–C2	1.425(12)
Fe–C3	2.059(9)	C1–C5	1.456(14)
Fe–C4	2.072(9)	C2–C3	1.404(14)
Fe–C5	2.004(9)	C3–C4	1.395(15)
Fe–C6	2.001(8)	C4–C5	1.405(16)
Fe–C7	2.027(9)	C6–C7	1.437(13)
Fe–C8	2.045(9)	C6–C10	1.448(13)
Fe–C9	2.057(9)	C7–C8	1.405(14)
Fe–C10	2.014(8)	C8–C9	1.397(17)
Si–C1	1.851(9)	C9–C10	1.407(19)
Si–C6	1.865(9)		
	Angles		
C1–Si–C6	95.7(4)	C11–Si–C12	114.8(6)
C1–Si–C11	111.9(5)	Si–C1–C2	121.5(6)
C1–Si–C12	111.4(5)	Si–C1–C5	119.9(6)
C6–Si–C11	111.8(6)	Si–C6–C7	119.7(6)
C6–Si–C12	109.6(5)	Si–C6–C10	119.1(7)

Table IV. Final Fractional Coordinates and Thermal Parameters for the Non-Hydrogen Atoms of 3

atom	x	y	z	U_{eq},[a] Å^2
Fe	0.53468(4)	0.00061(4)	0.33776(4)	0.04275(22)
Si1	0.52857(6)	−0.09377(7)	0.15016(4)	0.0377(3)
Si2	0.37569(6)	0.10598(7)	0.14845(4)	0.0404(4)
C1	0.61296(22)	−0.12288(28)	0.26157(15)	0.0451 (12)
C2	0.71251(25)	−0.0240(4)	0.31268(18)	0.0557(16)
C3	0.7281(3)	−0.0631(5)	0.39514(20)	0.0689(20)
C4	0.6406(4)	−0.1842(4)	0.39631(18)	0.0717(20)
C5	0.5700(3)	−0.2220(3)	0.31528(17)	0.0600(17)
C6	0.38743(22)	0.12763(27)	0.25861(15)	0.0448(13)
C7	0.4795(3)	0.2236(3)	0.31653(20)	0.0605(17)
C8	0.4787(4)	0.1815(4)	0.39569(19)	0.0723(21)
C9	0.3890(3)	0.0604(5)	0.38906(19)	0.0716(20)
C10	0.33171(25)	0.0265(4)	0.30556(17)	0.0558(16)
C11	0.4419(3)	−0.2737(4)	0.10525(24)	0.0615(18)
C12	0.6595(3)	−0.0436(4)	0.10059(22)	0.0634(19)
C13	0.4284(4)	0.2893(4)	0.11084(29)	0.0768(24)
C14	0.19882(29)	0.0592(5)	0.09074(22)	0.0621(19)

[a] $U_{eq} = (U_{11} + U_{22} + U_{33})/3$.

Table V. Selected Bond Lengths (Å) and Angles (deg) for 3 (Estimated Standard Deviations Are in Parentheses)

	Distances		
Fe–C1	2.0462(25)	Si2–C6	1.8762(26)
Fe–C2	2.0379(28)	Si2–C13	1.866(4)
Fe–C3	2.042(4)	Si2–C14	1.862(4)
Fe–C4	2.040(4)	C1–C2	1.432(4)
Fe–C5	2.0311(29)	C1–C5	1.432(4)
Fe–C6	2.0485(24)	C2–C3	1.423(5)
Fe–C7	2.027(3)	C3–C4	1.398(5)
Fe–C8	2.040(4)	C4–C5	1.411(4)
Fe–C9	2.041(4)	C6–C7	1.431(4)
Fe–C10	2.0355(28)	C6–C10	1.431(4)
Si1–Si2	2.3535(9)	C7–C8	1.416(5)
Si1–C1	1.8769(26)	C8–C9	1.392(6)
Si1–C11	1.858(3)	C9–C10	1.416(4)
Si1–C12	1.866(4)		
	Angles		
C1–Si1–Si2	102.84(8)	C2–C1–Si1	125.60(20)
C11–Si1–Si2	111.93(12)	C5–C1–Si1	126.99(20)
C12–Si1–Si2	114.02(12)	C12–Si1–C11	109.77(17)
C6–Si2–Si1	102.81(8)	C13–Si2–C6	109.20(16)
C13–Si2–Si1	111.54(14)	C14–Si2–C6	108.58(14)
C14–Si2–Si1	113.90(13)	C7–C6–Si2	126.38(20)
C11–Si1–C1	109.55(14)	C10–C6–Si2	126.57(19)
C12–Si1–C1	108.43(14)	C14–Si2–C13	110.43(20)

The Fe–Si distance in 1 (2.690(3) Å) is significantly greater than the sum of the covalent radii (2.37 Å) and the values reported for Fe–Si bonds (2.30–2.36 Å) but is consistent with the presence of a weak dative interaction on the basis of work by Silver.[27] The Si–Si bond length in 3 (2.3535(9) Å) is fairly normal for a single bond and is similar to that in Fe(η-$C_5H_4SiMe_2SiMe_3$)$_2$ (2.34(1) Å).[26] The methyl groups attached to silicon in the disilane bridge of 3 are virtually eclipsed with C11–Si1–Si2–C14 and C12–Si1–Si2–C13 torsion angles of 7.85(18)° and 8.34(19), respectively. Interestingly, the disilane bridge in 3 is significantly twisted and the Si–Si bond makes an angle of 8.4(4)° with the plane containing the centroids on the cyclopentadienyl rings and the iron atom. In addition, the C(Cp)–Si–Si bond angles in 3 (average 102.83(8)°) are significantly smaller than in Fe(η-$C_5H_4SiMe_2SiMe_3$)$_2$, where the corresponding angles are 107.9(11)° (average). In both 1 and 3 the cyclopentadienyl ligands are virtually planar. Thus, for 1 $\chi^2 = 4.2$ for the weighted least-squares plane through the cyclopentadienyl ligand containing C1–C5 and $\chi^2 = 2.2$ for the analogous C6–C10 plane. For 3 the corresponding values of χ^2 are 0.7 and 1.6. In addition, the cyclopentadienyl ligands in 1 are virtually eclipsed, with an angle of 0.4(5)° between the projection of the Fe–C bonds on the mean plane of the cyclopentadienyl rings. In contrast, in 3 the cyclopentadienyl ligands are slightly staggered with a corresponding angle of 6.0(1)°. This staggering is also reflected in the value for the C1–Si1–Si2–C6 torsion angle in 3, which is 8.07(11)°.

The molecular structure of 1 is comparable to that of the analogous species 4 and 5 (see Table VI). Thus, the tilt angle α between the cyclopentadienyl ligands in 1 is 20.8(5)°, which is slightly greater than the corresponding values in 4 and 5, which are 19.1(10) and 19.0(2)°, respectively. This is also reflected in the greater deviation of the Cp–Fe–Cp angle δ from 180° for 1, where the value is 164.74(8)°, compared to 167.3(6)° in 4 and 166.3(1)° in 5. Greater distortion in 1 is also apparent in the C(Cp)–Si–C(Cp) angle θ, where the value is 95.7(4)° compared to 99.2(5)° in 4 and 100.70(14)° in 5. In contrast, the value for β in 1 (37.0(6)°) is significantly less than that in 4 (40.0(9)°) or 5 (40.96(2)°).

The structure of 3 is interesting to compare to that of 6, the analogous species with a dicarbon bridge. Because the atomic size of carbon is significantly less than that of silicon, the length of the C–C bond in the bridge in 6 is only 1.58(1) Å compared to the length of the Si–Si bond in 3 (2.3535(9) Å). For the same reason, the C(Cp)–C bonds in 6 (average length 1.545(14) Å) are also shorter than the C(Cp)–Si bonds in 3 (average length 1.8765(26) Å). These

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[27] Silver, J. *J. Chem. Soc., Dalton Trans.* **1990**, 3513.

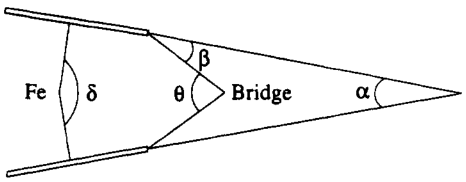

Figure 3. Distortions in ferrocenophanes defining angles α, β, δ, and θ.

effects cause the tilt angle α between the cyclopentadienyl ligands in **6** (23(1)°) to be much greater than that in **3** (α = 4.19(2)°). In addition, the Cp–Fe–Cp angle δ for **6** (163.4(6)°) shows a dramatically greater deviation from 180° compared to that for **3** (δ = 176.48(3) Å). Indeed, the deviation from 180° for **6** is slightly greater than that for **1**, where the value for δ is 164.74(8)°. In **6** the displacement of the iron atom from the line joining the two centroids of the cyclopentadienyl ligands (0.432(12) Å) is significantly greater than the value in **3** (0.027(3) Å). In contrast, the angles between the planes of the cyclopentadienyl ligands and the C(Cp)–C bonds (β) in **6** are 10.4(10) and 8.9(13)°, which is approximately the same as for **3** (10.8(3)°). Interestingly, the dicarbon bridge in **6** makes an angle of 18.4(1)° with the plane containing the centroids on the cyclopentadienyl rings and the iron atom and is therefore significantly more twisted than the disilane bridge in **3**, where the corresponding angle is 8.4(4)°. Overall, these structural data are clearly indicative of a much more strained structure for **6** compared to that for **3** and indeed suggest that **6** might be an interesting candidate for future polymerization studies.

Conclusions

The cyclic ferrocenylsilane **1** undergoes thermal ring-opening polymerization in the melt, whereas, under the same conditions, the cyclic ferocenyldisilane **3** does not polymerize. This difference in polymerization behavior can be explained by the different degrees of ring strain present in these two compounds. Thus, **1**, which possesses a strain energy of ca. 80 kJ mol^{-1} according to thermochemical measurements,[8a] possesses a distorted, ring-tilted structure as determined by X-ray diffraction. In contrast, the structure of **3** was found to be only slightly distorted and the ring tilt is significantly less.

Experimental Section

Materials. Dimethyldichlorosilane, trimethylchlorosilane, sodium metal, potassium metal, ferrocene, 1.6 M butyllithium in hexanes, and tetramethylethylenediamine (TMEDA) were purchased from Aldrich. The dichlorodisilane $ClMe_2SiSiMe_2Cl$ was prepared via the reaction of $Me_3SiSiMe_3$ with Me_3SiCl in the presence of $AlCl_3$.[19] The synthesis of $Me_3SiSiMe_3$ involved the reaction of Me_3SiCl with sodium–potassium alloy.[20]

Equipment. All reactions and manipulations were carried out under an atmosphere of prepurified nitrogen using either Schlenk techniques or an inert-atmosphere glovebox (Vacuum Atmospheres), except for the purification of polymer **2**, which was carried out in air. Solvents were dried by standard methods, distilled, and stored under nitrogen over activated molecular sieves. The 200- or 400-MHz ^1H NMR spectra and 50.3- or 100.5-MHz ^{13}C NMR spectra were recorded on a Varian Gemini 200 or a Varian XL 400 spectrometer, respectively. The 39.7-MHz ^{29}Si NMR spectra 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. All NMR spectra were referenced internally to TMS. Mass spectra were obtained with the use of a VG 70-250S mass spectrometer operating in an electron impact (EI) mode. Molecular weights were estimated by gel permeation chromatography (GPC) using a Waters Associates liquid chromatograph equipped with a Model 510 HPLC pump, a Model U6K injector, Ultrastyragel columns with a pore size between 10^3 and 10^5 Å, and a Waters Model 410 differential refractometer. A flow rate of 1.0 mL/min was used, and the eluent was a solution of 0.1% tetra-*n*-butylammonium bromide in THF. Polystyrene standards were used for calibration purposes. Elemental analyses were performed by the Canadian Microanalytical Service Ltd., Delta, BC, Canada. UV/visible spectra were recorded on a Hewlett-Packard 6452A diode array spectrophotometer using a 1-cm cell: the ϵ values quoted have the units M^{-1} cm^{-1}.

Synthesis of the Cyclic Ferrocenylsilane 1 and the Cyclic Ferrocenyldisilane 3. Compound **1** was prepared by the method reported by Wrighton[14] and was purified by high-vacuum sublimation (50 °C, 0.05 mmHg). Compound **3** was prepared by a modification of literature procedures,[18] as reported previously by us,[8b] and was purified by recrystallization from hot hexanes. Both compounds afforded ^1H, ^{13}C, and ^{29}Si NMR spectra, mass spectra, and melting points which are consistent with those reported in the literature either previously by others[14,18] or recently by us[8b] or are given below. Additional data for **1**: ^{29}Si NMR (in C_6D_6) δ −4.6 ppm; ^{13}C NMR (in C_6D_6) δ 77.7 (Cp), 75.6 (Cp), 33.5 (C–Si), −3.3 ppm ($SiMe_2$). Additional data for **3**: UV/vis (300–600 nm in hexanes) 324 nm (ϵ = 62) and 444 nm (ϵ = 88).

Ring-Opening Polymerization of 1: Synthesis of the Poly(ferrocenylsilane) 2. A sample of **1** (2.00 g, 8.26 mmol) was polymerized in an evacuated, sealed Pyrex tube at 130 °C for 1 h. A marked increase in viscosity was observed, and after 10 min the tube contents were immobile. Heating was then continued for a further 50 min. The polymeric product was dissolved in THF (40 mL) over 4 h, and this solution was then transferred via cannula to a stirred solution of hexanes (500 mL). The resulting suspension was stirred for 20 min. After the polymer was allowed to settle out, the mother liquors were then decanted. The polymer was then dried, redissolved in THF (30 mL), and precipitated into acetone (500 mL). The yellow, fibrous material was then dried in vacuo. The yield was 1.80 g (90%). Data for polymer **2**: ^{29}Si NMR (in C_6D_6) δ −6.4 ppm; ^{13}C NMR (in C_6D_6) δ 73.6 (Cp), 71.9 (Cp C–Si), 71.8 (Cp), −0.5 ppm ($SiMe_2$); ^1H NMR (in C_6D_6) δ 4.25 (br s, 4H, Cp), 4.10 (br s, 4H, Cp), 0.53 (s, 6H, $SiMe_2$) ppm; GPC $M_w = 5.2 \times 10.^5$, $M_n = 3.4 \times 10^5$, polydispersity (M_w/M_n) 1.5. Anal. Calcd: C, 59.5; H, 5.8. Found: C, 58.8; H, 5.6.

Attempted Ring-Opening Polymerization of the Cyclic Ferrocenyldisilane 3. (a) Ca. 0.5-g (1.7-mmol) samples of **3** were heated in evacuated, sealed Pyrex glass tubes at temperatures of (i) 150 °C, (ii) 200 °C, (iii) 250 °C, and (iv) 340 °C for 3 days. No increase in melt viscosity was noted, and the tube contents (dissolved in $CDCl_3$) were found to contain only unreacted **3** by ^1H NMR. In addition, analysis by GPC in THF showed that no high-molecular-weight material ($M_w > 1000$) was present.

(b) Ca. 0.4-g (1.3-mmol) samples of **3** together with ca. 1 mol %) of $K[OSiMe_3]$ were heated in evacuated sealed Pyrex glass tubes at (i) 140 °C for 1 h, (ii) 160 °C for 20 h, and (iii) 200 °C for 5 h. In all cases no increase in melt viscosity was observed and the tube contents (dissolved in $CDCl_3$) were subsequently found to contain only unreacted **3** by ^1H NMR. In addition, analysis by GPC showed that no high-molecular-weight material ($M_w > 1000$) was present.

(c) To a solution of **3** (1.0 g, 3.3 mmol) in THF (20 mL) was added ca. 0.1 mL (ca. 5 mol %) of a BuLi solution (1.6 M) in hexanes. After 3 days the reaction mixture was quenched with $SiMe_3Cl$ and the solvent and other volatiles were removed under vacuum. Analysis of the residual solid (dissolved in $CDCl_3$) showed only the presence of unreacted **3** by ^1H NMR, and analysis by GPC showed that no high-molecular-weight material ($M_w > 1000$) was present. A similar reaction utilizing 20 mg (5 mol %) of $K[OSiMe_3]$ in the place of BuLi gave the same results.

Table VI. Selected Structural Data for [1]- and [2]Ferrocenophanes (Estimated Standard Deviations Are in Parentheses)

	1	3	4	5	6
Fe–Si dist, Å	2.690(3)		2.636(5)	2.5931(1)	
Fe displacement,[a] Å	0.2164(11)	0.027(3)	0.183(12)	0.196(5)	0.432(12)
ring tilt, α, deg	20.8(5)	4.19(2)	19.1(10)	19.0(2)	23(1)
β,[b] deg	37.0(6)	10.8(3)	40.0(9)	40.96(2)	9.6(12)
C1–Si–C6, θ, deg	95.7(4)		99.2(5)	100.70(14)	
Cp–Fe–Cp, δ, deg	164.74(8)	176.48(3)	167.3(6)	166.3(1)	163.4(6)
ref	this work	this work	12	15	25

[a] The displacement of the iron atom from the line joining the two centroids of the cyclopentadienyl rings. [b] The average of the two angles between the planes of the cyclopentadienyl ligands and the C(Cp)–E bonds (where E = bridging atom).

X-ray Structure Determination Technique. Crystals of 1 decomposed rapidly when removed from a nitrogen atmosphere, whereas crystals of 3 were air-stable. The crystal of 1 used for this analysis was mounted on a glass fiber and coated with epoxy glue. Both crystals had dimensions in the range 0.25–0.45 mm. Intensity data for the compounds were collected on an Enraf-Nonius CAD-4 diffractometer at room temperature, using graphite-monochromated Mo Kα radiation (λ = 0.710 73 Å). The ω–2θ scan technique was applied with variable scan speeds. Intensities of three standard reflections were measured every 2 h. These showed no decay for 3, but the data for 1 were corrected for a linear intensity decay of 23%. The space groups were determined by systematic absences. An empirical absorption correction[28] was applied in both cases (maximum and minimum corrections 1.126 and 0.606 for 1 and 1.158 and 0.849 for 3).

The positions of the non-hydrogen atoms for both 1 and 3 were determined by direct methods using SHELX86.[29] For both structures all non-hydrogen atoms were refined anisotropically by full-matrix least-squares to minimize $\sum w(F_o - F_c)^2$, where $w^{-1} = \sigma^2(F) + gF^2$. For compound 1 the hydrogen atoms were positioned on geometric grounds (C–H = 0.95 Å, U(H) = U(C) + 0.01 Å^2), and in 3 the hydrogen atoms were refined with isotropic thermal parameters. Crystal data, details of data collection, and least-squares parameters are listed in Table I. Details of the molcular geometry are given in Tables II–VI. Figures 1 and 2 are views of the molecules prepared using ORTEP. Atomic scattering factors were taken from ref 32. All calculations were carried out on an Apollo computer using SHELX86,[29] SHELX76,[30] and NRCVAX.[31]

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Supplementary Material Available: Tables of complete bond lengths and angles, anisotropic thermal parameters, hydrogen atom coordinates, torsion angles, and least-squares plane data and figures showing the molecular structures of 1 and 3 (13 pages). Ordering information is given on any current masthead page.

OM920527N

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