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Ferrocenylsiloxane Chemistry: Synthesis and Characterization of Hexaferrocenylcyclotrisiloxane and Tetraferrocenyldisiloxanediol

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Base-catalyzed condensation of diferrocenylsilanediol, $Fc_2Si(OH)_2$ (**3**; Fc = (η-C_5H_4)Fe(η-C_5H_5)), in refluxing 95% ethanol (ca. 90 °C) affords a novel cyclotrisiloxane with six ferrocenyl substituents, $[Fc_2SiO]_3$ (**4**), in 74% yield. At 60 °C, the intermediate tetraferrocenyldisiloxanediol, $[HOSiFc_2]_2O$ (**5**), could be isolated in 78% yield. NMR, IR, Raman, and UV−vis data for **4** and **5** were consistent with the proposed structures. Electrochemical studies of **4** showed that there are substantial interactions between the ferrocenyl groups attached to the same Si atom and weaker interactions between the ferrocenyl groups attached to adjacent Si atoms. Furthermore, single-crystal X-ray diffraction studies of these compounds revealed an essentially planar Si_3O_3 ring in **4** and a novel hydrogen-bonded chain motif for disiloxanediol **5**. Surprisingly, **4** and **5** cocrystallize in a 1:3 ratio from a CH_2Cl_2/hexanes mixture to afford an interesting helical hydrogen-bonding structure for the siloxanediol **5**.

Introduction

The incorporation of transition elements into polymeric structures is attractive, as it may allow the combination of the interesting physical properties of metals with the solubility and processibility of polymers.[1,2] Recent advances in the field suggest that materials with unique mechanical and physical properties may be obtained in this way. Unfortunately, synthetic routes to high-molecular-weight transition-metal-containing polymers are still generally underdeveloped. Our group has been exploring ring-opening polymerization (ROP) of cyclic inorganic rings as a route to well-characterized, high-molecular-weight polymers.[3]

Poly(siloxanes) (silicones), $[R_2SiO]_n$, are appealing polymers for many applications as a consequence of their chemical stability, low toxicity, high gas permeability, and insulating characteristics.[4,5] For example, this class of inorganic polymers can be found in sealants, contact lenses, coatings, and a variety of biomedical applications.[6] The most practical route to high-molecular-weight poly(siloxanes) (e.g. poly(dimethylsiloxane), PDMS) is through the ROP of cyclic siloxane trimers and tetramers rather than the hydrolytic condensation of dichlorosilanes, which generally yields only oligomers and low-molecular-weight polymers.[4b]

The thermal stability and interesting electrochemistry of ferrocene make it an attractive moiety to incorporate into polysiloxanes.[7,8] Attachment of ferrocenyl substituents to a polysiloxane chain may allow electrochemical control of the polymer properties such as gas permeability as well as modification of other chemical and mechanical characteristics. Indeed, several groups have

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(1) For recent examples of transition-metal-based polymeric materials, see, for example: (a) *Metal-Containing Polymeric Materials*; Pittman, C. U., Carraher, C. E., Zeldin, M., Sheats, J. E., Culbertson, B. M., Eds.; Plenum Press: New York, 1996. (b) Altman, M.; Bunz, U. H. F. *Angew. Chem., Int. Ed. Engl.* **1995**, *34*, 569. (c) Rosenblum, M.; Nugent, H. M.; Jang, K.-S.; Labes, M. M.; Cahalane, W.; Klemarczyk, P.; Reiff, W. M. *Macromolecules* **1995**, *28*, 6330. (d) Chen, H.; Archer, R. D. *Macromolecules* **1995**, *28*, 1609. (e) Stanton, C. E.; Lee, T. R.; Grubbs, R. H.; Lewis, N. S.; Pudelski, J. K.; Callstrom, M. R.; Erickson, M. S.; McLaughlin, M. L. *Macromolecules* **1995**, *28*, 8713. (f) Buretea, M. A.; Tilley, T. D. *Organometallics* **1997**, *16*, 1507. (g) Southard, G. E.; Curtis, M. D. *Organometallics* **1997**, *16*, 5618.

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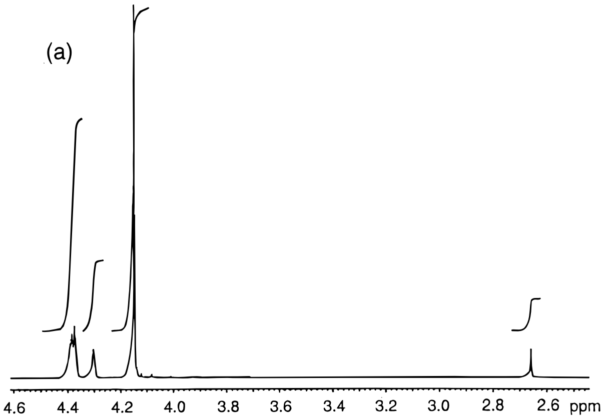
recently reported poly(siloxanes) with ferrocene-containing moieties on the side chains.[8] As these materials have all been prepared by grafting ferrocene-containing precursors onto a polysiloxane backbone, they suffer from the difficulties inherent with incomplete substitution and potential complications arising from a nonhomogeneous distribution of ferrocene-containing substituents in the polymer. Furthermore, the ferrocene substituents, which are separated from the siloxane backbone by an organic spacer, are unable to interact electrochemically. Thus, we targeted cyclic siloxanes with ferrocenyl side groups or siloxane-bridged ferrocenophanes as suitable precursors for ROP.[9]

To date, however, very few cyclic siloxanes with redox-active substituents have been prepared. Star polymers with a cyclotetrasiloxane core and oligoferrocenylsilane arms have been recently prepared by a transition-metal-catalyzed, grafting, ROP reaction.[10] Prior to this, Cuadrado and co-workers have also reported the synthesis of silsesquioxanes functionalized with ferrocenylethyldimethylsiloxyl groups and cyclotetrasiloxanes substituted with ethylferrocenyl groups.[11] We identified silanediol **3** as a convenient precursor to cyclosiloxanes with ferrocenyl substituents. In this paper, we report the synthesis and characterization of a novel cyclotrisiloxane with six ferrocenyl substituents, $[Fc_2SiO]_3$ (**4**; Fc = $(\eta\text{-}C_5H_4)Fe(\eta\text{-}C_5H_5)$). An intermediate in the condensation, $[HOSiFc_2]_2O$ (**5**), has been isolated and characterized. Moreover, an interesting cocrystallization of **4** and **5** has been discovered and examined by single-crystal X-ray diffraction.

Results and Discussion

Synthesis and Characterization of Hexaferrocenylcyclotrisiloxane (4). We have recently reported a convenient, high-yield (>88%) synthesis of diferrocenyldichlorosilane, Fc_2SiCl_2 (**2**), via treatment of the spirocyclic [1]silaferrocenophane, fc_2Si (**1**; fc = $(\eta\text{-}C_5H_4)_2Fe$), with HCl.[12] The subsequent hydrolysis of **2** provided access to diferrocenylsilanediol, $Fc_2Si(OH)_2$ (**3**), in 90% yield.[12] After **3** was refluxed in 95% ethanol for 2.5 h, the reaction mixture contained only the single new product **4** by ^1H NMR spectroscopy. After isolation, this air-stable, orange crystalline compound was identified as the cyclotrisiloxane **4**.[13] The ^1H NMR spectrum of the product showed two pseudo-triplets and a singlet for the Cp ligands. In the ^{13}C NMR spectrum, four resonances were observed, with the *ipso* resonance at 67.4 ppm. The ^{29}Si NMR spectrum of **4** showed only a single resonance at −26.2 ppm (C_6D_6), slightly upfield from the resonance observed in silanediol **3** (−25.1 ppm in DMSO-d_6). Mass spectrometry gave the molecular ion (*m/z* 1242) as the major peak. In addition, UV−vis spectroscopy and elemental analysis were consistent with the proposed structure.



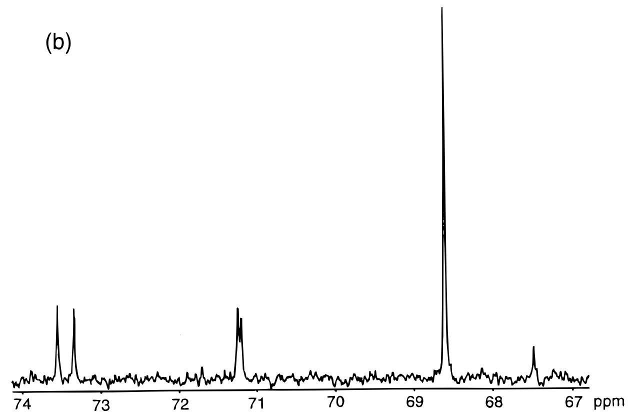


Figure 1. (a) ^1H NMR (400 MHz) and (b) ^{13}C NMR (100.5 MHz) of tetraferrocenyldisiloxanediol (**5**) in $CDCl_3$, showing splitting of the resonances attributed to the Cp rings as a result of the asymmetry in the molecule.

To investigate the thermal stability of **4**, differential scanning calorimetry (DSC) and thermogravimetric analysis (TGA) were performed. DSC showed no transitions below 250 °C (under N_2). By TGA, compound **4** is stable to over 300 °C under nitrogen, showing a ca. 50% weight loss between 300 and 500 °C. The ceramic product obtained at 900 °C was attracted to a bar magnet.

Synthesis and Characterization of Tetraferrocenyldisiloxanediol (5). Silanols, which are more acidic and reactive than alcohols, are key intermediates in the hydrolytic condensation of chlorosilanes to form low-molecular-weight poly(siloxanes). These species are generally unstable but can be isolated as solids only under very stringent conditions or where the substituents at Si are bulky. Furthermore, silanols are known to assemble into fascinating hydrogen-bonded structures in the solid state.[14]

When silanediol **3** was heated to 60 °C in ethanol for 10 min, a new product was isolated. The mass spectrum of the yellow-orange product showed a peak at *m/z* 846, suggesting that the compound was the disiloxanediol $[HOSiFc_2]_2O$ (**5**). The ^1H and ^{13}C NMR spectra, however, showed doubling of the cyclopentadienyl CH resonances that is consistent with two different ferrocenyl groups

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[13] For a recent example of a hexaferrocenyl arene iron complex, see Fillaut, J.-L.; Linares, J.; Astruc, D. *Angew. Chem., Intl. Ed. Engl.* **1994**, *33*, 2460.

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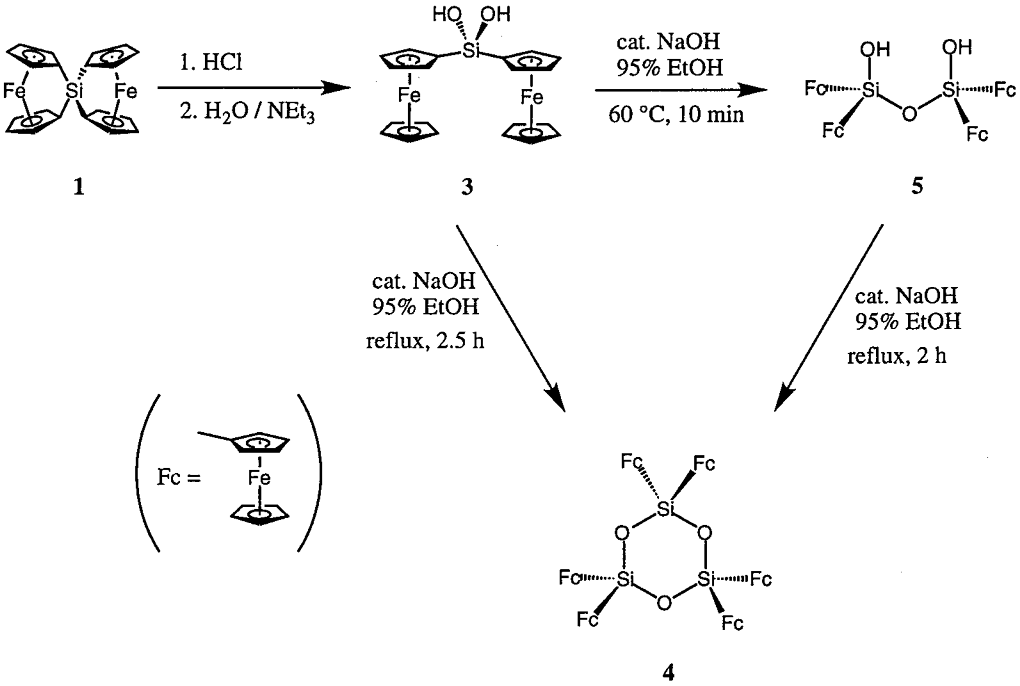
Scheme 1



in the structure (Figure 1). These initially unanticipated spectra can be rationalized by the unsymmetrical environment of the silicon atoms. Specifically, the absence of a mirror plane passing through the cyclopentadienyl ligands and the Si atom to which they are attached renders the protons of the Cp ligand inequivalent. The ^{1}H NMR resonance for the OH protons of the siloxanediol was observed at 2.66 ppm in $CDCl_3$ and appears to be independent of concentration. The ^{29}Si NMR spectrum of **5** shows a resonance at −25.6 ppm ($CDCl_3$), which is almost the same as in compound **4**. UV−vis spectroscopy and elemental analysis were also consistent with the proposed structure of disiloxanediol **5**.

Scheme 1 shows the synthetic pathway to compounds **4** and **5** from the spirocyclic [1]silaferrocenophane **1**. To prove that siloxanediol **5** was indeed an intermediate in the synthesis of cyclotrisiloxane **4**, a sample of pure **5** was heated in 95% ethanol in the presence of NaOH. The primary product formed in the reaction was **4**, confirming that **5** is an intermediate in the condensation of siloxanediol **3** to give **4**. This reaction must proceed by a base-catalyzed rearrangement of the siloxane, possibly involving a cyclotetrasiloxane intermediate which we have been unable to isolate. Rearrangements of this type are well-known in siloxane chemistry.[15]

Vibrational Spectra of Cyclotrisiloxane 4 and Disiloxanediol 5. To corroborate the structures of **4** and **5**, IR and Raman spectra were obtained. Both Raman and IR spectra of the compounds confirmed the presence of ferrocenyl moieties in the structure; the major peaks are identified in Table 1. Peaks attributed to cyclopentadienyl modes and ring deformation were assigned by comparison with ferrocene and the spirocyclic [1]ferrocenophanes.[16,17] The antisymmetric Si−O stretch in cyclotrisiloxane **4** was observed at 1015 cm^{-1} (Nujol and CCl_4) by IR but was not observed in the Raman spectrum. For comparison, hexaphenylcyclotrisiloxane shows two bands due to Si−O stretching at 1015 and 1032 cm^{-1}.[18] There may be a second Si−O stretch present near 1032 cm^{-1}, but it would overlap with the intense out-of-plane C−H bending mode of the cyclopentadienyl ligands. In the disiloxanediol **5**, the Si−O antisymmetric stretches are observed at 1099 and 1051 cm^{-1}. This is similar to the situation found for other siloxanediols; for example, the Si−O stretching vibration of tetraphenyldisiloxanediol is observed at 1078 cm^{-1}.[19a] The Si−OH stretch of the disiloxanediol was observed as a medium-intensity peak at 864 cm^{-1}, in agreement with other silanols.[19b] It was not possible to identify the symmetric ν(Si−O) mode expected in the 450−630 cm^{-1} region for **4** and **5**. Figure 2 shows the IR spectrum of the O−H stretching region for disiloxanediol **5** in the solid state. Notably, in the solid state there is a sharp absorption due to free O−H observed at 3605 cm^{-1} together with a very broad peak between 3300 and 3600 cm^{-1} (center at ca. 3470 cm^{-1}), consistent with hydrogen-bonded OH groups. In solution (CCl_4), however, there is only a single resonance due to free O−H stretching and it is observed at 3676 cm^{-1}, typical of disiloxanediols.[14]

Electrochemical Studies of Hexaferrocenylcyclotrisiloxane (4). To the best of our knowledge, studies revealing the electrochemical interaction of ferrocenyl substituents separated by a siloxane unit have not been reported. The differential pulse voltam-

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Table 1. Observed Infrared and Raman Frequencies (cm^{-1}) for Selected Vibrational Modes of 4 and 5

	4		**5**	
assignt[a]	IR[b]	Raman[c]	IR[b]	Raman[c]
ν(O−H) (free)			3605 (s)	
ν(O−H) (H-bonded)			3470 (s, b)	
ν(C−H)	3083 (s)	3105 (s), 3083 (s)	3102−3071 (s)	3105 (s), 3095 (s)
ν(C−C) sym			1423 (m)	1422 (m)
ν(C−C) sym	1413 (w)	1413 (m)	1414 (w)	1415 (m)
		1382 (m)		1382 (m)
ν(C−C)	1368 (m)	1367 (m)	1367 (m)	1367 (m)
ν(C−C)	1350 (w)	1353 (w)	1351 (w)	1353 (w)
	1185 (m)	1190 (m)	1187 (w)	
δ(C−H) ip	1167 (s)	1167 (s)	1168 (s)	1169 (s)
asym ring breath.	1107 (m)	1108 (s)	1106 (s)	1107 (s)
ν(Si−O) asym	1015 (s)		1099 (s), 1051 (m)	
δ(C−H) oop	1060 (w)	1061 (m)	1063 (w)	1063 (m)
δ(C−H) ip	1034 (s)	1036 (m)	1035 (s)	1036 (m)
δ(C−H) ip		1002 (w)	1001 (m)	1002 (w)
ring distortion	890 (w)	892 (m)	902 (m)	894 (w)
ν(Si−OH)			864 (m)	
δ(C−H) oop	836 (m)		838 (m)	
δ(C−H) oop	815 (m)	822 (w)	816 (s)	822 (w)
	734 (m)	734 (w)		
δ(C−C) oop	636 (m)	629 (w)	625 (m)	624 (w)
δ(C−C) oop	580 (m)	593 (w)		594 (w)
ring tilt		402 (m)		404 (w)
ring tilt		391 (w)		392 (m)
ν(Fe−Cp) sym		327 (s)		321 (s)

[a] Legend: ν = stretch; δ = bend; ip = in plane; oop = out of plane; w = weak; m = medium; s = strong. [b] Nujol mull. [c] Crystalline sample.

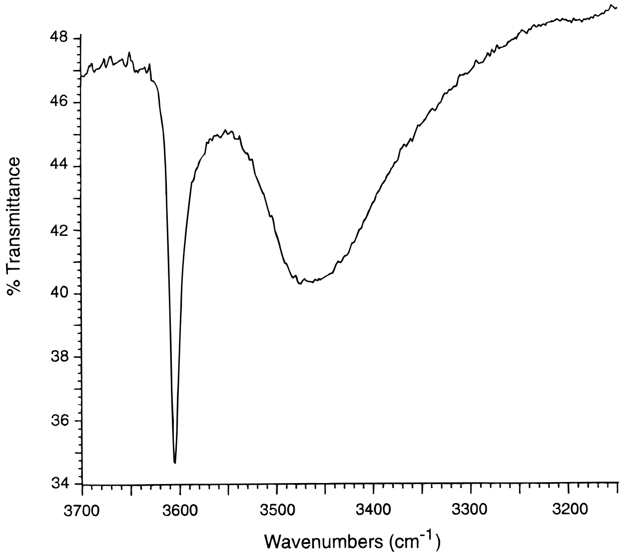

Figure 2. IR spectrum of the O−H stretching region for disiloxanediol **5** in a Nujol mull.

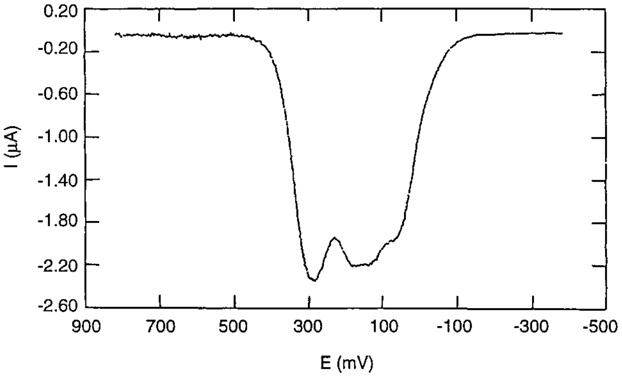

Figure 3. Differential pulse voltammogram of hexaferrocenylcyclotrisiloxane (**4**) (benzonitrile).

metry of **4** in benzonitrile shows several oxidation waves, as illustrated in Figure 3. We believe that the first wave between 0 and 250 mV (referenced to ferrocene) can be attributed to the oxidation of three Fc substituents, i.e., one Fc substituent attached to each Si atom. We assign the peak near 300 mV to the oxidation of the remaining three ferrocenyl substituents. These are expected to occur at higher potential, as oxidation of the second Fc attached to a single Si atom must result in significant Coulombic repulsion between the cations. Interestingly, the first oxidation wave shows fine structure attributed to overlapping oxidation waves of the first three Fc centers on adjacent Si atoms. This electronic interaction ($\Delta E \leq$ ca. 0.1 V) is comparable to the coupling observed between two ferrocenyl groups joined by a trisilane bridge ($\Delta E = 0.08$ V).[20]

Single-Crystal X-ray Diffraction (SCXRD) Studies. As relatively few single-crystal structures of cyclotrisiloxanes have been reported (none possessing ferrocenyl substituents), we undertook an investigation of the structure of the hexaferrocenylcyclotrisiloxane **4**. Single crystals suitable for SCXRD were obtained from warm dichloromethane. Data collection and refinement parameters for **4** are summarized in Table 2. Selected bond lengths and angles from the siloxane ring of **4** are provided in Table 3.

Compound **4** crystallizes in the triclinic $P\bar{1}$ space group with $Z = 4$. The two independent molecules of the asymmetric unit (A and B) are shown in Figure 4. In both molecules, the siloxane rings are essentially planar with mean deviations of 0.015 and 0.022 Å in molecules A and B, respectively. The sum of the interior angles of the two rings are 719.7(12) and 719.5(12)°, in good agreement with the expected sum of 720° for a planar six-atom ring. In both molecules, the Fc substit-

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Table 2. Crystal Data for Compounds 4, 5, and the Cocrystal

	4	5	cocrystal
empirical formula	$C_{60}H_{54}Fe_6O_3Si_3 \cdot 0.5CH_2Cl_2$	$C_{40}H_{38}Fe_4O_3Si_2$	$C_{201}H_{216}Cl_6Fe_{18}O_{12}Si_9$
M_r	1284.86	846.28	4294.55
temp (K)	110.0(1)	293(2)	203(2)
wavelength (Å)	0.710 73	0.710 73	0.710 73
cryst syst	triclinic	monoclinic	rhombohedral
space group	$P\bar{1}$	Cc	$R3$
a, Å	13.6449(7)	17.8040(3)	32.6448(4)
b, Å	20.3600(13)	14.6140(4)	32.6448(4)
c, Å	20.6260(12)	13.4620(2)	15.5290(2)
α, deg	113.068(1)	90	90
β, deg	90.290(1)	94.777(3)	90
γ, deg	94.286(1)	90	120
V, Å^3	5253.5(5)	3490.48(12)	14331.84(18)
Z	4	4	3
D_{calcd}, g cm^{-3}	1.624	1.610	1.493
μ(Mo Kα), mm^{-1}	1.780	1.737	1.518
$F(000)$	2628	1736	6642
crystal size (mm)	0.20 × 0.15 × 0.12	0.32 × 0.31 × 0.29	0.4 × 0.4 × 0.4
θ range collected, deg	4.15−26.46	4.34−26.40	1.95−28.26
total no. of rflns	37 536	13 591	21 800
no. of unique rflns	19 878	6805	11 648
R_{int}	0.050	0.0538	0.0261
abs cor	Denzo-SMN	Denzo-SMN	none
wR2 (all data)	0.1584	0.1186	0.1219
R1 ($I > 2\sigma(I)$)	0.0562	0.0342	0.0417
GOF	1.020	1.153	1.476
abs structure param		0.23(2)	0.023(16)
no. of params	1298	444	676
res electron density (e Å^{-3})	+0.720, −1.160	+0.396, −0.465	+1.583, −1.295
extinction coeff	0.0018(2)	0.0027(4)	0

Table 3. Selected Bond Lengths (Å) and Bond Angles (deg) for Cyclotrisiloxane 4

Bond Lengths

Si(1A)−O(1A)	1.641(4)	Si(1B)−O(1B)	1.638(4)
Si(1A)−O(3A)	1.633(3)	Si(1B)−O(3B)	1.629(4)
Si(1A)−C(1A)	1.837(6)	Si(1B)−C(1B)	1.839(6)
Si(1A)−C(11A)	1.838(6)	Si(1B)−C(11B)	1.835(6)
Si(2A)−O(1A)	1.634(4)	Si(2B)−O(1B)	1.634(4)
Si(2A)−O(2A)	1.638(4)	Si(2B)−O(2B)	1.632(4)
Si(2A)−C(21A)	1.843(6)	Si(2B)−C(21B)	1.835(6)
Si(2A)−C(31A)	1.832(6)	Si(2B)−C(31B)	1.836(6)
Si(3A)−O(2A)	1.639(4)	Si(3B)−O(2B)	1.641(4)
Si(3A)−O(3A)	1.640(4)	Si(3B)−O(3B)	1.642(4)
Si(3A)−C(41A)	1.842(6)	Si(3B)−C(41B)	1.838(6)
Si(3A)−C(51A)	1.830(6)	Si(3B)−C(51B)	1.830(6)

Bond Angles

Si(1A)−O(1A)−Si(2A)	133.2(2)
Si(1A)−O(3A)−Si(3A)	133.8(2)
Si(2A)−O(2A)−Si(3A)	133.7(2)
O(1A)−Si(1A)−O(3A)	106.43(19)
O(1A)−Si(2A)−O(2A)	106.5(2)
O(2A)−Si(3A)−O(3A)	106.02(19)
C(1A)−Si(1A)−C(11A)	116.2(3)
C(21A)−Si(2A)−C(31A)	115.7(3)
C(41A)−Si(3A)−C(51A)	114.9(2)
Si(1B)−O(1B)−Si(2B)	133.3(2)
Si(1B)−O(3B)−Si(3B)	133.6(2)
Si(2B)−O(2B)−Si(3B)	133.7(2)
O(1B)−Si(1B)−O(3B)	106.41(19)
O(1B)−Si(2B)−O(2B)	106.6(2)
O(2B)−Si(3B)−O(3B)	105.81(19)
C(1B)−Si(1B)−C(11B)	116.0(3)
C(21B)−Si(2B)−C(31B)	114.9(3)
C(41B)−Si(3B)−C(51B)	115.2(3)

uents are arranged in two opposing pinwheels that rotate counterclockwise when viewed on top of the siloxane ring. The Fe atoms of the ferrocenyl substituents attached to the same Si center are separated by 5.44−5.64 Å. For ferrocenyl substituents on adjacent Si atoms, however, the Fe centers are separated by 6.88−7.29 Å for the cis-adjacent ferrocenyl groups and 6.71−9.40 Å for the trans-adjacent ferrocenyl groups. From these values, it is expected that metal−metal interactions would be most significant for ferrocenyl moieties attached to the same Si atom.

The ferrocenyl substituents in the molecule are all slightly tilted, with ring tilts of 0.6−3.8° between the planes of the cyclopentadienyl ligands. This may be a result of the steric demands present in the molecule. In other respects, the ferrocenyl substituents are similar to ferrocene, with normal C−C bond lengths and Fe−Cp distances (1.637(3)−1.651(3) Å).

Hydrogen bonding in disiloxanediols may lead to intriguing double-chain structures.[14] Several simple disiloxanes of the general formula $(HOR_2Si)_2O$ (R = Me, Et, ^{n}Pr, ^{i}Pr, c-C_5H_9, Ph) have been structurally characterized and assemble into three simple motifs. As no diffraction studies of disiloxanediols with bulky ferrocenyl substituents have been undertaken, we investigated compound **5** by single-crystal X-ray diffraction. Data collection and refinement parameters for **5** are given in Table 2. Selected bond lengths, intermolecular distances, and angles for **5** are provided in Table 4.

Compound **5** crystallizes in the monoclinic space group *Cc*. The molecular structure of **5** is illustrated in Figure 5. Notably, the Si−O−Si angle is 157.1(3)°, similar to that observed in other siloxanediols.[14] When the molecule is viewed along the Si···Si axis, the substituents are approximately halfway between staggered and eclipsed, the torsion angle ω for O1···Si1···Si2···O2 being 31.5°.[21] Small ring tilts (1.8−3.0°) are present between the Cp ligands of the ferrocenyl substituents and may be the result of steric demands in the crystal packing. The Fe···Fe separations vary from 6.09 and 6.10 Å for ferrocenyl groups on the same Si

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(21) The torsion angle (ω) of A···B···C···D is defined as the angle between vector BA and vector CD when viewed down BC. ω is positive if BA must be rotated clockwise into CD and is negative if the rotation is counterclockwise.

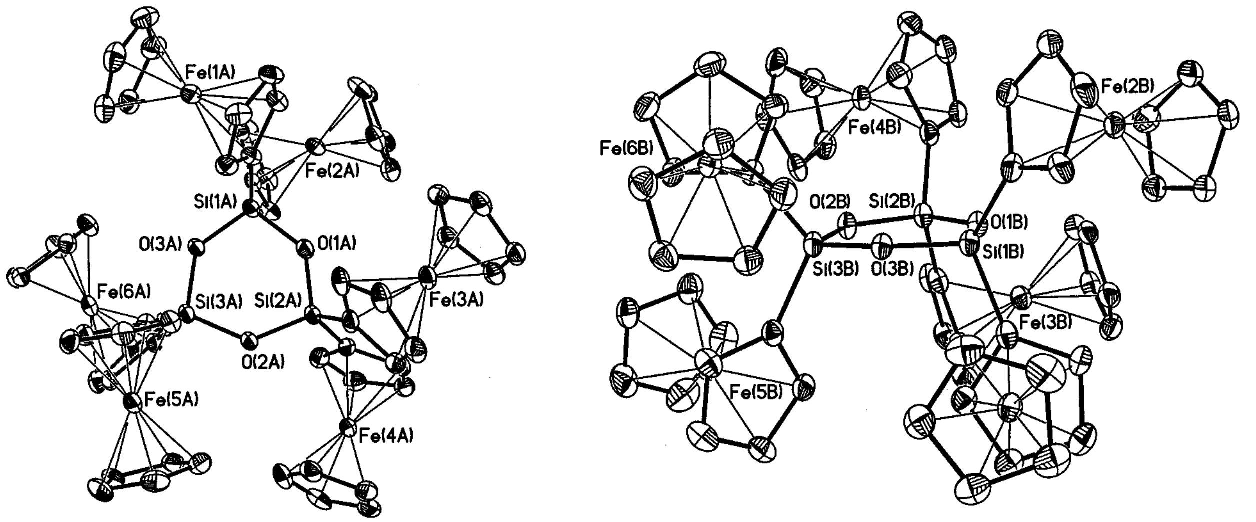

Figure 4. Molecular structure of hexaferrocenylcyclotrisiloxane (**4**). Both molecules (A and B) are shown with thermal ellipsoids at the 30% probability level.

Table 4. Selected Bond Lengths (Å), Intermolecular Distances (Å), and Bond Angles (deg) for Disiloxanediol 5

Bond Lengths			
Si(1)−O(1)	1.635(4)	Si(2)−O(2)	1.644(4)
Si(1)−O(3)	1.606(4)	Si(2)−O(3)	1.621(3)
Si(1)−C(1)	1.845(5)	Si(2)−C(11)	1.834(5)
Si(1)−C(21)	1.843(6)	Si(2)−C(31)	1.843(5)
Intermolecular Distances			
O(1)··· O(2)	2.931(4)	O(1)···O(1)	2.921(4)
Bond Angles			
O(1)−Si(1)−O(3)	107.7(2)	O(2)−Si(2)−O(3)	110.9(2)
C(1)−Si(1)−C(21)	112.0(2)	C(11)−Si(2)−C(31)	114.8(2)
Si(1)−O(3)−Si(2)	157.1(3)		

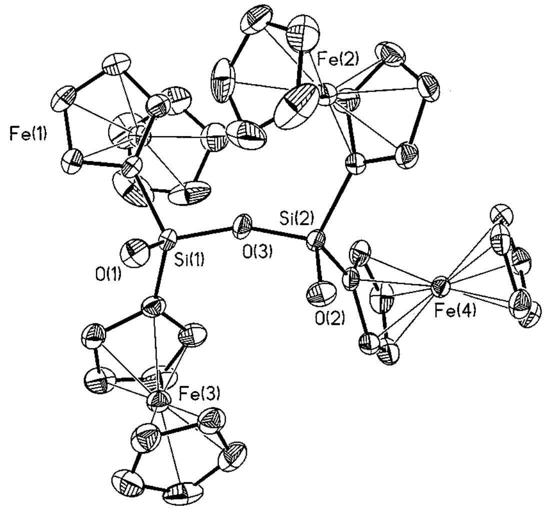

Figure 5. Molecular structure of tetraferrocenyldisiloxanediol (**5**). The molecule is shown with ellipsoids at the 30% probability level.

atom to 7.54 and 7.84 Å for ferrocenyl groups attached to different Si atoms.

The disiloxanediol packs into a hydrogen-bonded double-chain structure parallel to the *c* axis. The arrangement is unique and has not been observed in other disiloxanediols with very bulky groups, $(HOR_2Si)_2O$ (R = ^{i}Pr, c-C_5H_9).[14] This novel hydrogen-bonding network is depicted in Chart 1. In this motif, only three-fourths of the protons participate in hydrogen bonding. Indeed, this is consistent with the IR spectrum of **5**, where a sharp O−H stretching mode attributed to free O−H is observed at 3605 cm^{-1} in addition to a broad absorption at 3470 cm^{-1} attributed to hydrogen-bonded O−H groups. Figure 6 shows the arrangement of the two hydrogen-bonded chains and intermolecular O···O distances. Figure 7 shows three projections of the unit cell, illustrating the orientation of the disiloxanediol chains.

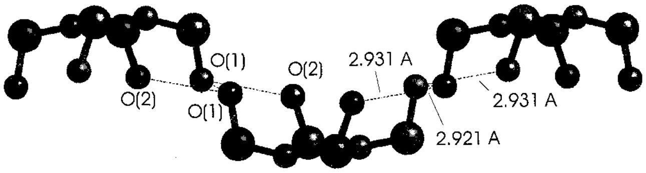

Figure 6. Segment of the hydrogen-bonded double chain present in compound **5**, showing the intermolecular O- - -O distances. The ferrocenyl substituents have been omitted for clarity.

The use of synthetic strategies to design and control the solid-state structure of materials, crystal engineering, is a current area of research in materials chemistry.[22] Cocrystallization is a fascinating method of controlling the solid-state conformation of molecules. From studies of cocrystals, one may also obtain information about the energy difference between conformations and the forces that direct the crystal packing. As an example, Pannell and co-workers have recently obtained structures of 1,1,3,3-tetramethyl-1,3-diferrocenyldisiloxane in the neat crystalline form and as a cocrystal with ferrocene and calculated the energy difference between the conformations observed.[23] During our attempts to grow single crystals from CH_2Cl_2/hexanes, we obtained a remarkable cocrystallization of cyclotrisiloxane **4** and disiloxanediol **5**. The cocrystallization incorporates **4** and **5** into a trigonal lattice (space group *R*3) in a 1:3 ratio along with a molecule of 3-methylpentane (from the hexanes) and CH_2Cl_2 in the asymmetric unit.

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(22) (a) *Supramolecular Architecture*; Bein, T., Ed.; ACS Symposium Series 499; American Chemical Society: Washington, DC, 1992. (b) Russell, V. A.; Ward, M. D. *Chem. Mater.* **1996**, *8*, 1654.

(23) Cervantes-Lee, F.; Sharma, H. K.; Pannell, K. H.; Derecskei-Kovacs, A.; Marynick, D. S. *Organometallics* **1998**, *17*, 3701.

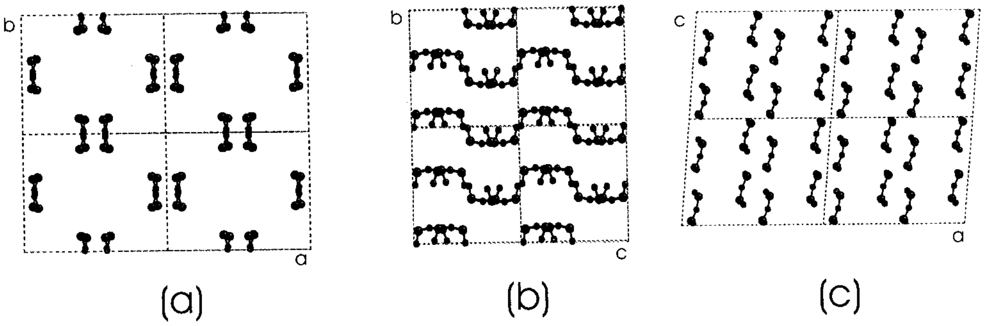
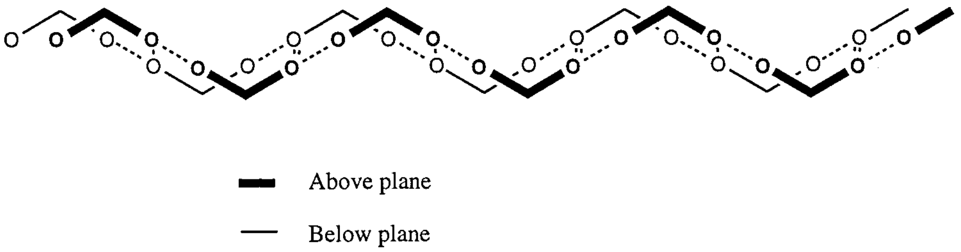


Figure 7. Projections of (a) the *ab* plane, (b) the *bc* plane, and (c) the *ca* plane in the structure of **5**, illustrating the hydrogen-bonded pairs of chains running parallel to the *c* axis. Ferrocenyl substituents have been omitted for clarity.

Chart 1



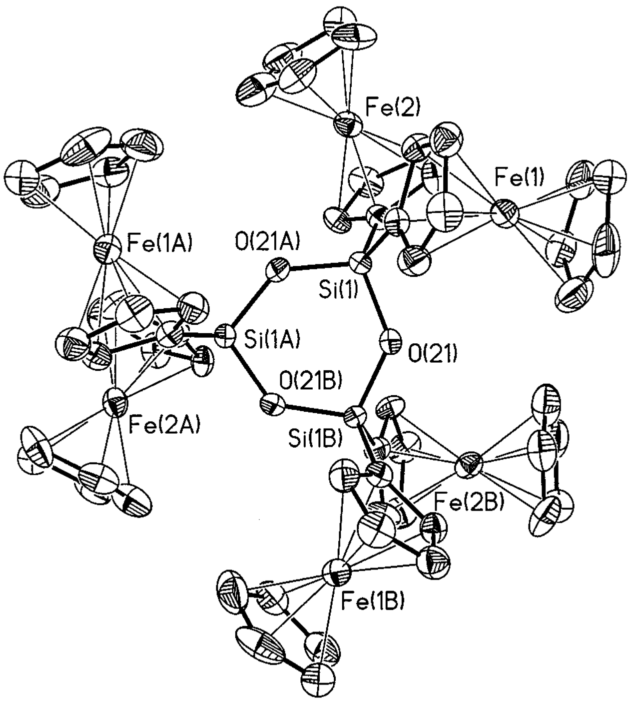


Figure 8. Molecular structure of hexaferrocenylcyclotrisiloxane (**4**) in the cocrystal. The molecule is shown with ellipsoids at the 50% probability level.

The ^{1}H NMR spectrum of the single crystals confirmed the presence of **4**, **5**, CH_2Cl_2, and hexanes, but resonances for 3-methylpentane could not be specifically resolved. The structure of the cyclotrisiloxane and the disiloxanediol in the cocrystal will be discussed in turn.

Figure 8 shows a view of cyclotrisiloxane **4** as crystallized in the cocrystal. Selected bond lengths and angles for **4** as observed in the cocrystal are summarized in Table 5. The cyclotrisiloxane ring lies on a 3-fold rotational axis. As in the pure compound, the Si_3O_3 ring observed in the cocrystal is essentially planar with a mean deviation of only 0.005 Å from planarity and an interior angle sum of 720(2)°, as predicted for a planar six-sided polygon. Although the ferrocenyl substituents are also arranged in two opposing pinwheels around the siloxane ring, they appear to be oriented differently from the structure of pure **4** with respect to the plane of the siloxane ring. In fact, the ferrocenes are oriented so that they rotate clockwise when viewed from the top of the siloxane ring; thus, the molecule is nearly a mirror image of the molecules observed in the crystal of pure **4**. The Fe atoms of the ferrocenyl substituents attached to the same Si centers are 5.404 Å apart, slightly closer than observed in crystals of pure **4**. The Fe atoms of cis-adjacent ferrocenyl substituents are 7.414 and 7.449 Å apart, whereas trans-adjacent ferrocenyl substituents show Fe- - -Fe separations of 6.790 and 9.534 Å.

Table 5. Selected Bond Lengths (Å) and Bond Angles (deg) for Cyclotrisiloxane 4 in the Cocrystal

Bond Lengths			
Si(1)−C(6)	1.859(8)	Si(1)−C(11)	1.828(8)
Si(1)−O(21)	1.636(5)		
Bond Angles			
Si(1)−O(21)−Si(1B)	133.4(3)	O(21)−Si(1)−O(21A)	106.6(3)
C(6)−Si(1)−C(11)	114.5(3)		

The structure of tetraferrocenyldisiloxanediol **5** as it appears in the cocrystal structure is illustrated in Figure 9. Selected bond lengths, intermolecular distances, and bond angles for **5** in the cocrystal are given in Table 6. As in the structure of pure **5**, the Si−O−Si angle is 157.1(3)°. However, the similarity between the two structures ends there. When viewed along the Si···Si axis, the substituents on the Si atoms appear more staggered in the cocrystal than observed in pure **5**. Indeed, the O71···Si2···Si3···O73 torsion angle (ω) is 48.2°, compared with 31.5° in the structure of pure **5** for the same measurement. As in the other structures, the ferrocenyl substituents exhibit small ring tilts (0.4−3.4°). Metal−metal separations vary from 5.91 and 5.94 Å for ferrocenyl groups on the same Si atom to 7.60 and 7.92 Å for ferrocenyl groups on adjacent Si atoms.

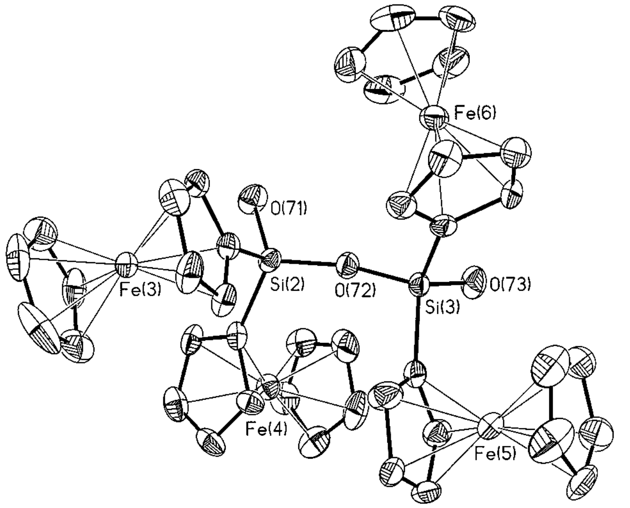


Figure 9. Molecular structure of tetraferrocenylcyclotrisiloxane (**5**) inside the cocrystal. The molecule is shown with thermal ellipsoids at the 50% probability level.

Table 6. Selected Bond Lengths (Å) and Bond Angles (deg) for Disiloxanediol 5 in the Cocrystal

Bond Lengths			
Si(2)−O(71)	1.643(5)	Si(3)−O(73)	1.635(5)
Si(2)−O(72)	1.620(6)	Si(3)−O(72)	1.630(6)
Si(2)−C(36)	1.856(7)	Si(3)−C(56)	1.865(7)
Si(2)−C(46)	1.849(7)	Si(3)−C(66)	1.870(7)
Intermolecular Distances			
O(71)···O(73)	10.566(6)	O(73)···O(73)	8.671(6)
O(71)···O(71)	8.427(6)	O(71)···O(73)	6.760(6)
O(71)···Cl(1)	3.279(5)	O(73)···Cl(2)	2.727(5)
O(71)···C(91)	2.748(7)	O(73)···C(91)	4.141(7)
Bond Angles			
O(71)−Si(2)−O(72)	109.4(3)	O(72)−Si(3)−O(73)	109.9(3)
C(36)−Si(2)−C(46)	107.0(3)	C(56)−Si(3)−C(66)	108.8(3)
Si(2)−O(72)−Si(3)	157.1(3)		

The disiloxanediol assembles into a fascinating 3-fold counterclockwise helical structure along the *c* axis. One helical chain is illustrated in Figure 10. Interestingly, there are no hydrogen bonds between the disiloxanediol molecules (the closest Si−O contacts are 6.760 Å), but dichloromethane molecules link the disiloxanediol molecules in the helix. Closest contacts between the O atom of the siloxanediol and the Cl atoms of dichloromethane are 2.727 and 3.279 Å, values that would be typical for hydrogen bonding. In addition, the close O(71)···C(91) contact (C(91) from CH_2Cl_2) of 2.748 Å suggests that there is hydrogen bonding between the O atom of the siloxanediol and the H atom of the dichloromethane.

Summary

Hexaferrocenylcyclotrisiloxane (**4**) and tetraferrocenyldisiloxanediol (**5**) were synthesized and characterized. Electrochemistry of **4** showed metal−metal interactions between ferrocenyl groups on adjacent Si atoms as well as the same Si atom. Single-crystal X-ray diffraction of **5** revealed a new double-chain hydrogen-bonding motif for disiloxanediols. A cocrystal of **4**, **5**, CH_2Cl_2, and 3-methylpentane was obtained from CH_2Cl_2/hexanes. The structures of **4** and **5** in the cocrystal were found to be similar to the structures of the pure compounds, but not identical. Indeed, **5** assembles into a 3-fold hydrogen-bonded helical structure linked with dichloromethane solvent molecules. Future work will involve studies of the ROP of **4** and related cyclic species.

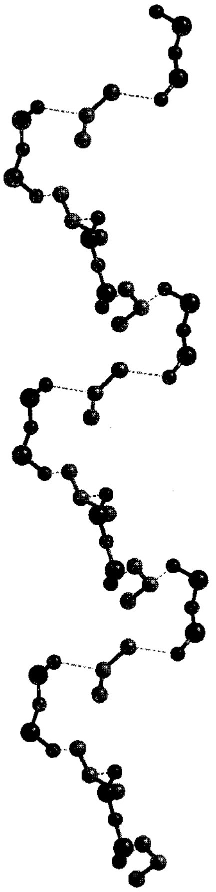


Figure 10. Structure of a helix formed by **5** with dichloromethane inside the cocrystal.

Experimental Section

Materials. Triethylamine was purchased from Aldrich and distilled from Na prior to use. Anhydrous 1 M HCl in diethyl ether and sodium hydroxide were purchased from Aldrich and used as received. The spirocyclic ferrocenophane **1**, dichlorodiferrocenylsilane (**2**), and diferrocenylsilanediol (**3**) were prepared by literature methods.[12,17]

Equipment. All reactions and manipulations were carried out under an atmosphere of prepurified nitrogen using either Schlenk techniques or an inert-atmosphere glovebox (Innovative Technologies) unless otherwise noted. Solvents were dried by standard methods, distilled, and stored under nitrogen. ^1H NMR spectra (400 MHz), ^{13}C NMR spectra (100.5 MHz), and ^{29}Si NMR spectra (79.5 MHz) were recorded on a Varian Unity 400 spectrometer and were referenced externally to TMS. UV−vis spectra were obtained in CH_2Cl_2 (ca. 5×10^{-4} M) on a Perkin-Elmer Lambda 900 UV−vis−near-IR spectrometer using a 1 cm quartz cuvette. IR spectra were obtained as Nujol mulls or CCl_4 solutions with a Nicolet Magna-IR 550 spectrometer. FT-Raman spectra were collected on a Bomem MB-157 FT spectrometer with a Spectra-Physics diode pumped Nd: YLF laser (1064 nm; 350 kHz repetition rate). The instrument was configured in 180° backscattering mode using sealed glass capillary tubes to hold the neat, crystalline samples. Electron impact (EI) mass spectra were obtained with a VG 70-250S mass spectrometer. Thermogravimetric analyses were obtained on a Perkin-Elmer TGA-7 analyzer equipped with a TAC-7 instrument controller. Samples were heated at a rate of 10 °C min^{-1} under a flow of N_2. Differential pulse voltammetry of **4** was performed under ambient conditions under N_2 by analysis of a 0.31 mM solution in benzonitrile on a PAR Model 174 potentiostat using 1 s drop time and 25 mV modulation amplitude settings. Potentials in this paper are given versus the ferrocene/ferrocenium couple. Melting points were determined on a Fisher-Johns hot-stage melting point apparatus and are uncorrected.

Synthesis of Hexaferrocenylcyclotrisiloxane (4). A mixture of diferrocenylsilanediol (**3**; 0.200 g, 0.463 mmol) and ca. 5 mL of 95% ethanol was refluxed at 95 °C, giving a yellow-orange solution. Three drops of 4 M NaOH (aqueous) were added, immediately giving an orange precipitate. The mixture was refluxed for an additional 2.5 h, giving a pale yellow solution and orange powder. After cooling at −55 °C, the product was isolated on a Buchner funnel (under air) and washed with cold ethanol. The yellow powder was dried under vacuum to afford 0.142 g (0.114 mmol; 74%) of cyclotrisiloxane **4**.

Data for 4: ^{13}C NMR (100.5 MHz, C_6D_6) δ 74.3 (Si−Cp), 71.9 (Si−Cp), 69.5 (Cp), 67.4 (*ipso*-Cp) ppm; ^{1}H NMR (400 MHz, C_6D_6) δ 4.85 (t, $^3J_{HH} = 1.65$ Hz, 12H, Cp), 4.35 (t, $^3J_{HH} = 1.65$ Hz, 12H, Cp), 4.18 (s, 30H, Cp) ppm; ^{29}Si NMR (79.5 MHz, C_6D_6) δ −26.2 ppm. UV−vis (CH_2Cl_2) λ_{max} 452 nm ($\epsilon = 665$ L mol^{-1} cm^{-1}); MS (EI, 70 eV) *m*/*z* (%) 1242 (100, M$^+$); dec pt >215 °C. Anal. Calcd: C, 58.00; H, 4.38; N, 0.00. Found: C, 57.80; H, 4.44; N, <0.05.

Synthesis of Tetraferrocenyldisiloxanediol (5). A 50 mL round-bottom flask was charged with 2.125 g (4.92 mmol) of **3** and 30 mL of 95% ethanol. The flask was then heated to ca. 80 °C to dissolve all of the silanediol. The solution was maintained at 60 °C in a water bath. While the mixture was stirred, 7 drops of 4 M NaOH(aq) were added and an orange precipitate formed immediately. The mixture was heated at 60 °C for an additional 10 min. After the mixture was cooled to −55 °C, the product (**5**) was collected on a Buchner funnel and washed with ca. 10 mL of cold ethanol. Yield: 1.630 g (1.93 mmol, 78%) of orange crystals.

Data for 5: ^{13}C NMR (100.5 MHz, $CDCl_3$) δ 73.55 (Si−Cp), 73.34 (Si−Cp), 71.24 (Si−Cp), 71.20 (Si−Cp), 68.6 (Cp), 67.5 (*ipso*-Cp) ppm; ^{1}H NMR (400 MHz, $CDCl_3$) δ 4.38 (m, 12H, Cp), 4.30 (m, 4H, Cp), 4.15 (s, 20H, Cp), 2.66 (s, 2H, OH) ppm; ^{29}Si NMR (79.5 MHz, $CDCl_3$) δ −25.6 ppm; UV−vis (CH_2Cl_2) λ_{max} 449 nm ($\epsilon = 481$ L mol^{-1} cm^{-1}); MS (EI, 70 eV) *m*/*z* (%) 846 (100, M$^+$); Mp 197−198 °C. Anal. Calcd: C, 56.77; H, 4.53; N, 0.00. Found: C, 56.81; H, 4.46; N, <0.05.

Conversion of Disiloxanediol 5 to Cyclotrisiloxane 4. A suspension of disiloxanediol **5** (100 mg, 0.118 mmol) in 20 mL of 95% ethanol was heated to reflux at ca. 90 °C. Three drops of 4 M NaOH(aq) solution were added, and the solution was refluxed for 2 h. After the mixture was cooled to room temperature, the yellow powder was isolated on a Buchner funnel and, after drying under vacuum, gave 0.042 g (0.034 mmol, 43%) of pure cyclotrisiloxane **4** by ^{1}H NMR. The yellow filtrate was evaporated to dryness, and ^{1}H NMR of the residue showed that it contained primarily the product **4** and unreacted **5**, with a small quantity of unidentified species.

Crystallographic Structural Determination. Selected crystal, data collection, and refinement parameters for **4**, **5**, and the cocrystal are given in Table 2. Selected inter- and intramolecular distances and bond angles for **4** and **5** are provided in Tables 3 and 4, respectively. Data for **4** and **5** were collected on a Nonius Kappa-CCD diffractometer using graphite-monochromated Mo Kα radiation ($\lambda = 0.710\ 73$ Å). The data from 180 × 1° ϕ scans were integrated and scaled using the Denzo-SMN package.[24] The structure was solved and refined using the SHELXTL/PC package.[25] Refinements were by full-matrix least squares on F^2 using all data (negative intensities included). All hydrogen atoms were included in calculated positions and treated as riding atoms except for the silanol hydrogens, which could not be located and, thus, were omitted for refinement. All non-hydrogen atoms were refined with anisotropic thermal parameters.

Suitable crystals of the cocrystal were grown from a mixture of CH_2Cl_2 and hexanes (ca. 1:1), were sectioned, and were mounted on thin glass fibers with epoxy cement. The data were collected on a Siemens P4 diffractometer equipped with a SMART/CCD detector. Selected inter- and intramolecular bond angles for **4** and **5** in the cocrystal are given in Tables 5 and 6, respectively.

The unit cell parameters, systematic absences, and occurrences of equivalent reflections in the cocrystal are consistent with the rhombohedral space groups $R\bar{3}$, $R3$, $R3m$, $R32$, and $R\bar{3}m$. The absence of a molecular mirror plane and a 2-fold rotation axis excluded space groups $R3m$, $R32$, and $R\bar{3}m$. Chemical composition suggested the space group $R3$, which yielded chemically reasonable and computationally stable results of refinement.

The structure was solved by direct methods, completed by subsequent difference Fourier syntheses, and refined by full-matrix least-squares procedures. Further refinement of the crystal structure showed signs of merohedral twinning; a [b, a, $-c$] transformation matrix was applied to resolve the twinning, which decreased the R factor from 14% to 5%. Hexaferrocenylcyclotrisiloxane is located on a 3-fold axis, and tetraferrocenyldisiloxanediol is in a general position. The asymmetric unit also contains a molecule of 3-methylpentane and one of dichloromethane. All non-hydrogen atoms of the solvent molecules were refined isotropically. The hydrogen atoms on the silanol oxygen atoms could not be located from the difference map and were ignored, and the hydrogen atoms on the dichloromethane carbon atom were ignored. The remaining hydrogen atoms were treated as idealized contributions. All other non-hydrogen atoms were refined with anisotropic displacement parameters.

All software and sources of the scattering factors are contained in the SHELXTL (5.1) program libraries (G. Sheldrick, Siemens XRD, Madison, WI).

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Supporting Information Available: Tables of complete bond lengths and angles, anisotropic thermal parameters, and atomic coordinates and figures showing the molecular structures of **4**, **5**, and the cocrystal. This material is available free of charge via the Internet at http://pubs.acs.org.

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