(Bis{2,4,6-triisopropylphenyl}stannylene)ferrocenophane and Related Ring-Opened Products

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The addition of bis(2,4,6-triisopropylphenyl)tin dichloride (**1**) to a hexane/THF slurry of 1,1′-dilithioferrocene−tmeda produces the corresponding stannyleneferrocenophane (**2**) in good yield. Structural analysis of **2** reveals a dihedral angle between the two cyclopentadienyl rings of 14.7° and a relatively short Fe−Sn atomic distance of 2.994(2) Å. Cyclic voltammetry of **2** exhibits reversible redox behavior. Whereas treatment with MeOH and H_2O failed to produce ring-opened compounds, silica gel catalyzed hydrolysis of **1** leads to ring-opened $Fc(i\text{-}Pr_3C_6H_2)_2SnOH$ (**3**), which crystallizes as a H-bonded dimer. Thermal treatment of **2** at 180 °C leads to the ring-opened polymerization product **4**, which after precipitation from toluene remains insoluble in organic solvents. Solid-state ^{13}C and ^{119}Sn NMR spectra of **4** confirm the structure of the material. The X-ray structural analysis of **1** is reported and compared to that of **2**.

Introduction

The reaction of 1,1′-dilithioferrocene with group 14 dihalides has long been known to yield [1]ferrocenophanes in the case of silicon and germanium[1−3] and polymeric materials and dimers in the case of tin.[4,5] The ability of singly bridged silyl- and germylferrocenophanes to undergo heat-, anion- or metal-catalyzed ring opening to form high-molecular-weight polymers is currently of some interest;[6−9] therefore, the synthesis and chemical properties of the group 14 bridged ferrocenophanes has been revisited. The Manners group recently reported the synthesis and structure of (di-*tert*-butylstannylene)ferrocenophane and its thermal ring opening at 150 °C to form polymers of high molecular weight; M_w = 133 000.[10]

We report the preparation of a stable (diarylstannylene)ferrocenophane (**2**) from the low-temperature reaction between 1,1′-dilithioferrocene and bis(2,4,6-triisopropylphenyl)tin dichloride (**1**) and its thermal ring-opening polymerization to yield an insoluble polymer (**4**). Silica gel hydrolysis of **2** yields the corresponding ferrocenyldiaryltin hydroxide **3**, and the structure of **3** is reported, along with those of **1** and **2**.

Experimental Details

All reactions were performed under an argon or nitrogen atmosphere with dry solvents. Solution NMR data were collected on a Bruker 200 MHz multinuclear spectrometer, and solid-state NMR data were collected on a Bruker 400 MHz spectrometer spinning at 13 kHz. Cyclic voltammetry was performed as previously described using CH_2Cl_2 solutions and tetraethylammonium tetrafluoroborate as supporting electrolyte, with an Ag/AgCl reference electrode.[8c]

Synthesis of (Bis{2,4,6-triisopropylphenyl}stannylene)-[1]ferrocenophane (2). 1,1′-Dilithioferrocene−tmeda obtained from 1.0 g of ferrocene (5.37 mmol) was dissolved in 40 mL of hexane and 20 mL of THF, and the mixture was maintained at −40 °C. Bis(2,4,6-triisopropylphenyl)tin dichlo-

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ride[11] (3.2 g, 5.37 mmol), dissolved in 10 mL of THF, was added by syringe at −40 °C. The reaction mixture was maintained at this temperature for 40 min and slowly brought to room temperature and stirred for 12 h at room temperature. The solvents were removed in vacuo, and the orange residue was extracted with 100 mL of toluene and filtered through Celite. The toluene was removed in vacuo, and the orange solid obtained was recrystallized from a 1:1 toluene−hexane mixture to yield **2** (2.29 g, 3.22 mmol, 60%). Anal. (Galbraith Laboratories Inc.) Calcd for $C_{40}H_{54}FeSn$: C, 67.72; H, 7.67. Found: C, 67.94, H, 7.83. ^1H NMR (ppm, C_6D_6): 1.19 (d, 12H, *p*-Me, $J = 6.8$ Hz); 1.34 (d, 24H, *o*-Me, $J = 6.4$ Hz); 2.76 (sept, 2H, *p*-CH, $J = 6.7$ Hz); 3.70 (sept, 4H, *o*-CH, $J = 6.4$ Hz); 4.38 (d, 4H, Cp); 4.43 (d, 4H, Cp); 7.19 (s, 4H, Ar H). ^{13}C NMR (ppm, C_6D_6): 24.1 (*p*-CH_3); 25.9 (*o*-CH_3); 34.6 (*p*-CH); 37.7 (*o*-CH); 38.8 (*ipso* C of C_5H_4); 76.6, 77.1 (C_5H_4); 122.5, 138.2, 150.7, 156.1 (Ar). ^{119}Sn NMR (ppm, C_6D_6): −129.5. ^{119}Sn NMR (ppm, solid state): −129.3.

Ring-Opening Polymerization of 2. A sample of **2** (0.4 g 0.56 mmol) was heated in an evacuated sealed Pyrex tube at 180 °C for 2 h. The red melt was dissolved in 10 mL of toluene over a period of 2 h. The polymeric solution was then added dropwise to 100 mL of stirred hexane, and a yellow polymer precipitated. This material was collected by filtration and dried in vacuo to yield the corresponding polymer (0.17 g, 42%). The polymer **4** was found to be insoluble in common organic solvents after the precipitation from toluene. ^{119}Sn NMR (ppm, solid state): −133.1, −142.2 (sh). ^{13}C (ppm, solid state): 24.9, 26.0 (CH_3); 34.8, 37.7 (CH); 39.1 (CH); 71.5, 75.1 (C_5H_4); 121.6, 122.9, 139.5, 142.8, 149.4, 155.1 (Ar).

Hydrolysis of (Bis{2,4,6-triisopropylphenyl)stannylene}[1]ferrocenophane (2). A sample of **2** (0.3 g, 0.42 mmol) was dissolved in 10 mL of a hexane/methylene chloride (1:1) solvent mixture and placed upon a 1.5 × 20 cm wet silica gel column. Elution with methylene chloride developed an orange band that was collected and, after solvent removal, produced an orange solid. The solid was recrystallized from hexanes to yield **3** (0.23 g, 0.316 mmol, 75%). Anal. (Galbraith Laboratories Inc.) Calcd for $C_{40}H_{56}FeOSn$: C, 66.04; H, 7.75. Found: C, 65.56, H, 8.08. ^1H NMR (ppm, $CDCl_3$): 0.57 (s, OH); 1.02 (d, 12H, CH_3, $J = 6.6$ Hz); 1.03 (d, 12H, CH_3, $J = 6.6$ Hz); 1.17 (d, 12H, CH_3, J = 6.9 Hz); 2.81 (sept, 2H, *p*-CH, $J = 6.9$ Hz); 3.16 (sept, 4H, *o*-CH, $J = 6.6$ Hz); 4.18 (s, 5H, Cp); 4.27 (t, 2H, Cp); 4.40 (t, 2H, Cp); 6.95 (s, 4H, Ar H). ^{13}C NMR (ppm, $CDCl_3$): 23.9, 24.6, 25.0 (CH_3); 34.2, 37.0 (CH); 68.4, 70.5, 73.2 (Cp); 78.9 (ipso-C of C_5H_4); 121.9, 139.6, 150.3, 154.9 (Ar). ^{119}Sn NMR (ppm, $CDCl_3$): −55.3. IR (cm^{-1}, hexane): 3642.5 (s, OH).

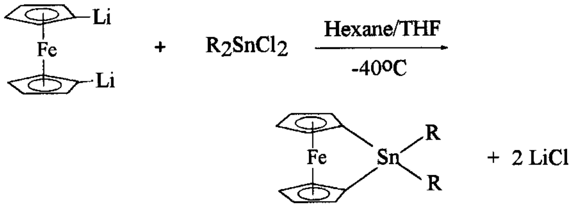
Structural Analyses of 1−3. A colorless fragment of **1** of approximate dimensions 0.36 × 0.50 × 0.40 mm was mounted in a random orientation at the tip of a glass fiber for X-ray examination and data collection. All data were collected at room temperature on a Siemens R3m/v single-crystal diffractometer with graphite-monochromated Mo Kα radiation; λ(Mo Kα) = 0.710 73 Å. Unit cell parameters and standard deviations were obtained by a least-squares fit of 25 randomly selected reflections in the 2θ range of 15−30°. They indicated monoclinic symmetry, which was confirmed by oscillation photographs around each crystallographic axis. Intensity data were collected in the ω-scan mode with a scan range of 1.2° in ω and a variable speed of 5−20° min^{-1}. Background counts were taken with a stationary crystal and a total background time to scan time ratio of 0.5. Three standard reflections were monitored every 197 reflections and showed an intensity decay of less than 3%, which was considered acceptable. The collection was conducted over slightly more than one quadrant of reciprocal space, in the range $-16 = h = 16$, $-2 = k = 14$, $-17 = l = 8$. A total of 5342 reflections were collected, which after merging equivalents produced a set of 2081 unique reflections with the reliability parameter $R_{int} = 3.6\%$. The data were corrected for Lorentz and polarization effects. A semiempirical absorption correction was also applied with a minimum/maximum transmission ratio of 0.3637/0.3970.

Structure Refinement. Analysis of the data set based on cell parameters, systematically absent reflections, and counting statistics led to selection of space group *C*2/*c* (No. 15). The structure was solved by the heavy-atom method and refined by full-matrix least squares, based on *F*, in a PC computer running the PC version of the SHELEXTL-PLUS software package by Siemens. The quantity minimized was $\sum w(F_o - F_c)^2$. All non-hydrogen atoms were placed at calculated positions with C−H bond distances of 0.96 Å and average isotropic thermal parameters of 0.08. The weighting scheme has the form $w^{-1} = \sigma^2(F) + gF^2$ with $g = 0.001$. The final *R* factors have the form $R = \sum|F_o - F_c|/\sum F_o$ and $R_w = [w|F_o - F_c|^2/\sum F_o^2]^{1/2}$. Reflections with intensities giving *F* values smaller than 2 times their standard deviation from their mean value were treated as unobserved. For the last cycle of refinement of 151 parameters and 2007 reflections, the maximum shift/σ was 0.902, the maximum and minimum residual electron densities were 0.43 and −0.37 e $Å^{-3}$, and the final *R* values, as defined above, were $R = 0.039$ and $R_w = 0.057$. No efforts were made to improve the R_w values by changing the weighting schemes.

Similar procedures and calculations were conducted for complexes **2** and **3.** Unit cell dimensions and other relevant crystallographic parameters and selected bond angles and bond lengths are presented in Tables 1 and 2.

Results and Discussion

The ability to isolate stannylene[1]ferrocenophanes depends on the bulk of the organic groups bonded to tin. Whereas 1,1′-dilithioferrocene reacts with di-*tert*-butyltin dichloride to form (di-*tert*-butylstannylene)ferrocenophane as a stable isolable material,[10] earlier attempts to form such compounds containing methyl, *n*-butyl, and phenyl groups led to dimeric and oligomeric materials.[4,5] The bulky bis(2,4,6-triisopropylphenyl)tin dichloride (**1**), first reported by Masamune and Sita,[11] has been used as a precursor for the formation of several interesting organotin systems due to its ability to impart kinetic stability to the products.[12] This, coupled with the potential of the isopropyl groups to improve the solubility of any polymers produced (the reported (diphenylstannylene)ferrocenylene polymer was insoluble in common organic solvents), led us to use this reagent for the synthesis of (bis(2,4,6-triisopropylphenyl)stannylene)ferrocenophane (**2**) via the reaction described in eq 1.



(1)

(R = 2,4,6-tri-isopropylphenyl)

The reaction produced a high yield of **2** as an orange crystalline material. All spectroscopic data are in accord with the expected structure, including the characteristic ^{13}C resonance for the *ipso*-cyclopentadienyl carbon atom

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Table 1. Crystallographic Parameters

	1	**2**	**3**
empirical formula	$C_{30}H_{46}Cl_2Sn$	$C_{40}H_{54}FeSn$	$C_{40}H_{56}FeOSn$
color; habit	colorless fragment	orange-red fragment	yellow fragment
cryst size (mm)	0.36 × 0.50 × 0.40	1.00 × 0.54 × 0.32	0.08 × 0.24 × 0.26
crystal syst	monoclinic	orthorhombic	triclinic
space group	$C2/c$	$P2_12_12_1$	$P\bar{1}$
unit cell dimens			
a, Å	15.404(4)	11.110(3)	11.018(3)
b, Å	13.071(2)	14.252(4)	12.792(2)
c, Å	16.453(3)	23.281(8)	15.209(3)
α, deg	90.00	90.00	66.55(2)
β, deg	107.09(2)	90.00	75.83(2)
γ, deg	90.00	γ = 90.00	82.95(2)
V, Å^3	3166.5(11)	3686(2)	1905.9(7)
Z	**4**	**4**	**2**
2θ range, deg	3.5−45	3.5−45	3.5−45
scan type	ω	ω	ω
scan speed, deg min^{-1}	5−20	4−20	4−15
scan range (w), deg	1.20	1.70	1.20
std rflns	3 measd every 197 rflns	3 measd every 197 rflns	3 measd every 197 rflns
index ranges	h from −16 to 16	h from 0 to 11	h from 0 to 10
	k from −2 to 14	k from 0 to 15	k from −12 to 12
	l from −17 to 17	l from −2 to 25	l from −14 to 14
no. of rflns collected	5342	6249	3837
no. of indep rflns	2081	4826	3586
no. of obsd rflns	2007 ($F > 2.0\sigma(F)$)	4639 ($F > 2.0\sigma(F)$)	2863 ($F > 4.0\sigma(F)$)
abs cor	semiempirical	semiempirical	not applied
min/max transmissn	0.364/0.397	0.107/0.183	n/a
final R indices (obsd data), %	R = 3.94, R_w = 5.73	R = 4.69, R_w = 6.12	R = 3.88, R_w = 4.79

Table 2. Selected Bond Lengths (Å) and Angles (deg) for 1−3

	Complex **1**		
Sn−Cl	2.353(2)	Sn−C(1)	2.147(4)
Sn−Cl(A)	2.353(2)	Sn−C(1A)	2.147(4)
Cl−Sn−C(1)	118.5(1)	Cl−Sn−Cl(A)	98.0(1)
C(1)−Sn−Cl(A)	100.1(1)	Cl−Sn−C(1A)	100.1(1)
C(1)−Sn−C(1A)	120.4(2)	Cl(A)−Sn−C(1A)	118.5(1)
	Complex **2**		
Sn···Fe	2.994(2)	Sn−C(1)	2.209(8)
Sn−C(6)	2.180(9)	Sn−C(11)	2.173(6)
Sn−C(26)	2.175(7)		
Fe−Sn−C(1)	43.0(2)	Fe−Sn−C(11)	42.9
C(1)−Sn−C(6)	85.9(3)	C(1)−Sn−C(11)	106.9(3)
C(6)−Sn−C(11)	121.9(3)	C(11)−Sn−C(26)	109.9(2)
	Complex **3**		
Sn−O	2.005(40)	Sn−C(1)	2.129(7)
Sn−C(11)	2.170(9)	Sn−C(26)	2.182(8)
O−Sn−C(1)	102.4(1)	O−Sn−C(11)	101.5(2)
C(1)−Sn−C(11)	120.8(3)	O−Sn−C(26)	113.8(3)

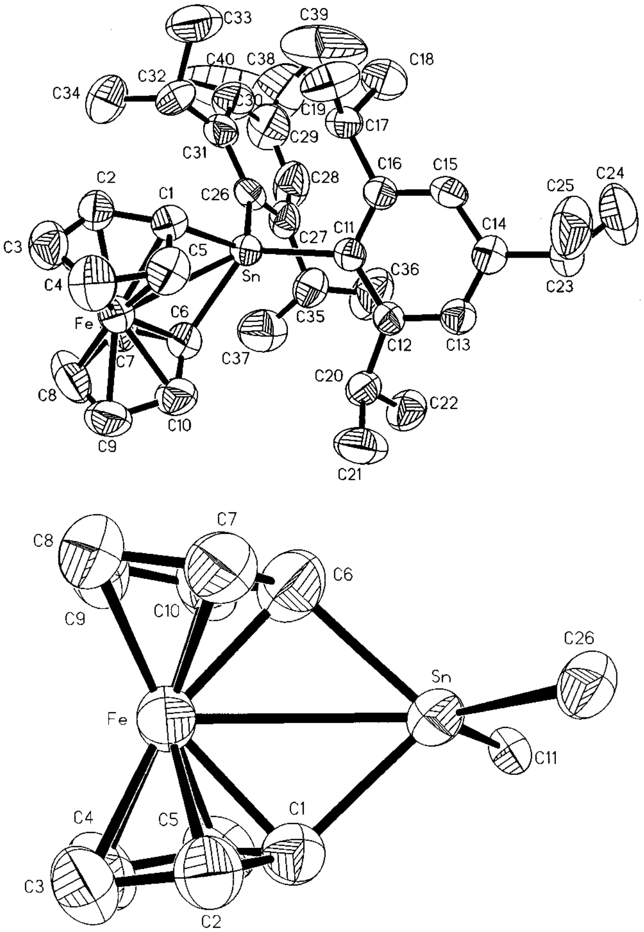

Figure 1. Structure of **2**: (a, top) general structure; (b, bottom) illustration of ring tilt.

at 38.8 ppm and a solution ^{119}Sn NMR resonance at −129.5 ppm. The single-crystal structure of **2** is illustrated in Figure 1 and may be compared to the structure of the dichloride **1** illustrated in Figure 2. The important features of the structure of **2** are the dihedral angle between the two cyclopentadienyl rings, 14.7°, the two Sn−C(cyclopentadienyl) bond lengths of 2.209(8) and 2.180(9) Å, and an Fe−Sn distance of 2.994(2) Å. These features of the structure are similar to the data for the analogous (di-*tert*-butylstannylene)ferrocenophane.[10] The geometry around the tin atom of **2** differs significantly from that around the Sn atom of **1**. Whereas **2** has a C(aryl)−Sn−C(aryl) bond angle (C(11)−Sn−C(26)) of 109.9°, the corresponding angle in **1** (C(1)−Sn−C(1a)) is 120.4°. The corresponding C(cyclopentadienyl)−Sn−C(cyclopentadienyl) angle in **2**, C(1)−Sn−C(6) = 85.9°, is also significantly smaller than the Cl−Sn−Cl bond angle of 98.0° in **1**. This latter bond angle, also significantly smaller than the "expected" tetrahedral angle, is in the range typical for organotin dichlorides, which range from 93° for Me_2SnCl_2 (which exhibits a considerable intermolecular Sn···Cl interac-

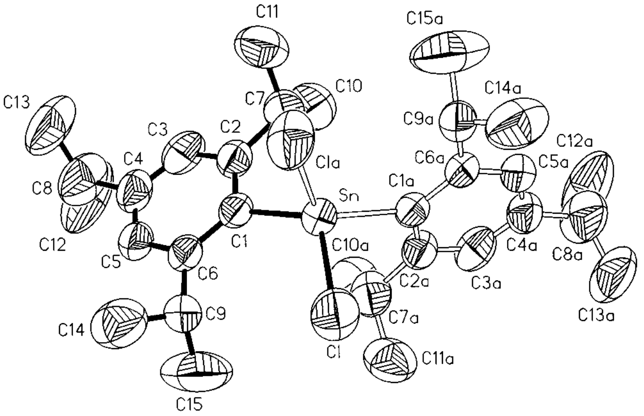

Figure 2. Structure of **1**.

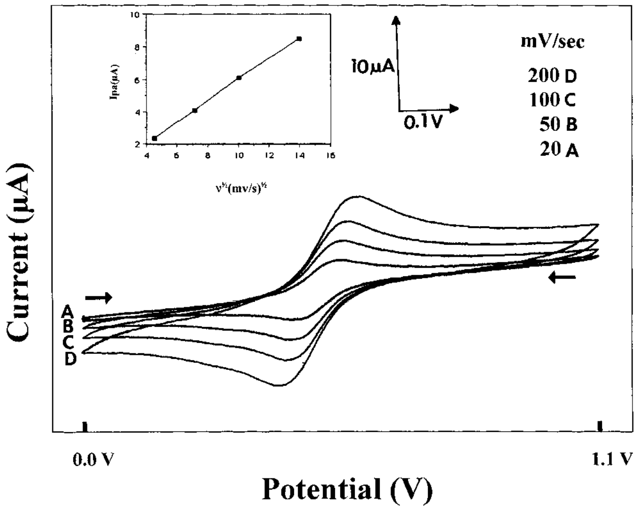

Figure 3. Cyclic voltammograms of **2** at varying scan rates.

tion, $Me_2SnCl_2\cdots Cl = 3.54$ Å[13]) to 102° in t-Bu_2SnCl_2, where minimum intermolecular interactions were noted (t-$Bu_2Cl_2Sn\cdots Cl > 4.0$ Å).[14a] In the present case the bulk of the triisopropylphenyl groups precludes any significant intermolecular association in the solid state and the closest such $Sn\cdots Cl$ intermolecular interaction is 7.7 Å, close to that of 6.5 Å in the closely related bis(2,4,6-tri-*tert*-butylphenyl)tin dichloride.[14b] The distortion from tetrahedral geometry about the tin atom in **1** seems therefore a typical feature of the organotin dihalides, even when intermolecular interactions are negligible.[14]

Cyclic voltammetric analysis of **2** (Figure 3) exhibits a pattern of reversible oxidation at the iron center, as noted for the di-*tert*-butyl analogue.[10] For example, with a scan rate of 50 mV/s, $E_{ox} = 0.55$ V (relative to Ag/Ag$^+$) and $E_{red} = 0.45$ V. Under similar experimental conditions the related (dimethylsilylene)[1]ferrocenophane exhibits a tendency for irreversibility, presumably due to the ring strain produced upon oxidation. It is established that the two cyclopentadienyl rings of ferrocene move apart upon formation of the ferrocenium ion.[15] Apparently the larger tin atom can better accommodate such ring expansion in this system (note dihedral angles of ~15° for the Sn ferrocenophanes as opposed to ~20° for the Si analogues), resulting in a greater stability of the oxidized stannyleneferrocenophane. It should be noted that at more rapid scan rates silyl[1]ferrocenophanes exhibit complete electrochemical reversibility;[6g] however, polarographic studies on ethylene[2]ferrocenophane in ethanol have been reported to exhibit irreversible oxidation.[19]

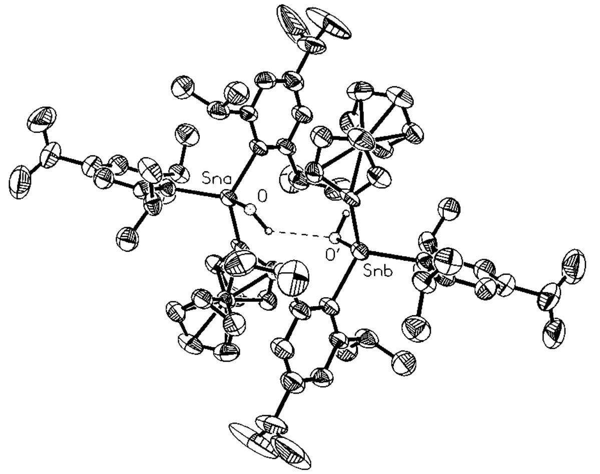

Figure 4. Structure of **3**.

Further evidence for the stability of **2** comes from its lack of reaction with methanol, up to reflux temperature, and water. This is in contrast to the behavior of (diphenylsilylene)[1]ferrocenophane, which reacts readily with MeOH to form $FcSiPh_2OMe$ and with water to form $FcSiPh_2OH$.[2,7f] More drastic hydrolysis conditions, chromatography of **2** on wet silica gel, do result in the formation of the ring-opened $FcSn(i$-$Pr_3C_6H_2)_2OH$ (**3**). The crystal structure of **3** was determined and is illustrated in Figure 4. The hydroxide forms an unusual dimeric structure via intermolecular H-bonding between the OH groups of adjacent molecules. This type of interaction is not common in tin hydroxides, and indeed there are only a few tetrahedral tin hydroxides reported in the Cambridge Crystallographic Data Base, since oligomeric structures predominate.[16] It is of interest that the closely related trimesityltin hydroxide reported by Reuter exhibits no evidence for H-bonding oligomerization.[17] However, a very recently published structure of $\{(Me_3Si)_2CH\}_2SnH(OH)$ has structure analogous to that of **3** involving dimerization via the hydroxyl groups.[18] The selected bond lengths and angles for **3** are presented in Table 2, and the $O\cdots O$ interatomic distance of 3.12 Å is slightly longer than that reported for $\{(Me_3Si)_2CH\}_2SnH(OH)$.[18]

Monitoring **2** by variable-temperature solid-state NMR (^{119}Sn NMR, −129.3 ppm) showed that it is stable up to 150 °C. However, efficient ring opening of **2** was accomplished at 180 °C in the solid state. The initially

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obtained polymer was soluble in toluene; however, after precipitation using hexane the resulting material, **4**, obtained as a pale yellow material, was insoluble in organic solvents (benzene, toluene, methylene chloride, and THF). This insolubility is typical of (diarylsilylene)- and (diarylgermylene)ferrocenylene polymers, and the isopropyl groups do not contribute to enhanced solubility. Solid-state NMR revealed the expected resonances for the polymer structure derived from a thermal ring opening of **2.** Of note are two resonances observed in the ^{119}Sn NMR spectrum, a major resonance at −133.1 and a small shoulder at −142.2 ppm, the latter possibly due to terminal Sn units. The major resonance at −133.1 ppm is slightly shifted to high field compared to that of the corresponding monomer **2** (−129.3 ppm). Such small high-field shifts are also observed in solid-state ^{29}Si NMR of the (diphenylsilylene)ferrocenylene polymer.[6c]

Powder X-ray diffraction analysis indicates that polymer **4** is a partially crystalline material and exhibits low-intensity peaks at 13.2 and 10.1 Å not typical of those silylene and germylene polymers, which can exhibit significant crystallinity.

The results of a TGA study on **2** and **4** are presented in Figure 5. The ferrocenophane commenced initial weight loss at 180 °C with a second phase of mass loss between 300 and 400 °C. The thermally ring-opened polymer **4** exhibited a single weight loss event between 300 and 400 °C. These data suggest that under the open conditions of the TGA experiment there is some initial decomposition of the monomer **2** involving mass loss of 40% concurrent with polymer formation. Both **2** and **4** exhibit a residual mass of between 15 and 20%.

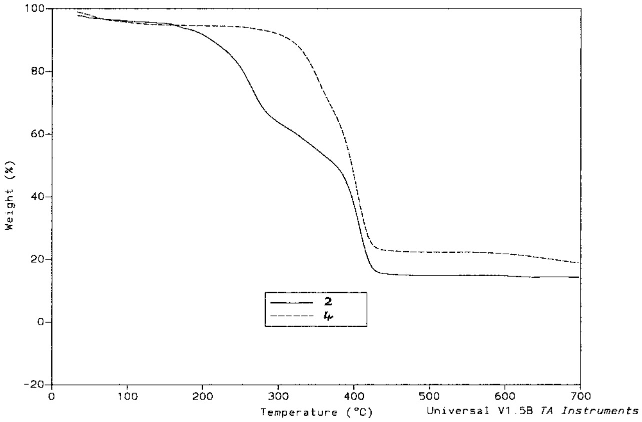

Figure 5. TGA data for **2** and **4** (heating at 1 °C/min; N_2 purge 100 mL/min).

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Supporting Information Available: Tables of crystal data, atomic coordinates, thermal parameters, and bond distances and angles for **1**−**3**. This material is available free of charge via the Internet at http://pubs.acs.org.

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