Thermal and Transition-Metal-Catalyzed Ring-Opening Polymerization (ROP) of [1]Silaferrocenophanes with Chlorine Substituents at Silicon: A Route to Tunable Poly(ferrocenylsilanes)

David L. Zechel, Kai C. Hultzsch, Ron Rulkens, David Balaishis, Yizeng Ni, John K. Pudelski, Alan J. Lough, and Ian Manners*

Department of Chemistry, University of Toronto, 80 St. George Street, Toronto M5S 1A1, Ontario, Canada

Daniel A. Foucher*

Xerox Research Centre of Canada, 2660 Speakman Drive, Mississauga L5K-2L1, Ontario, Canada

The silicon-bridged [1]ferrocenophanes $Fe(\eta\text{-}C_5H_4)_2SiRR'$ [**3** (R = Me, R′ = Cl), **4** (R = R′ = Cl)] with chlorine substituent(s) at silicon were prepared via the reaction of $Fe(\eta\text{-}C_5H_4\text{-}Li)_2 \cdot TMEDA$ (TMEDA = tetramethylethylenediamine) with the chlorinated silanes $MeSiCl_3$ and $SiCl_4$, respectively. An X-ray diffraction study of **4** indicated that the cyclopentadienyl rings in this species are tilted by an angle of 19.2(4)°, typical of other structurally characterized silicon-bridged [1]ferrocenophanes. Thermal ring-opening polymerization (ROP) of **3** and **4** at 250 °C yielded the first high molecular weight poly(ferrocenylsilanes) with halogen substituents at silicon, $[Fe(\eta\text{-}C_5H_4)_2SiRR']_n$ [**7** (R = Me, R′ = Cl), **8** (R = R′ = Cl)]. Transition-metal-catalyzed polymerization of **3** and **4** with Pd and Pt catalysts also yielded polymers **7** and **8** in solution at room temperature. Polymer **7** was soluble in polar organic solvents and was characterized by ^1H, ^{29}Si, and ^{13}C NMR and elemental analysis. In contrast, poly(ferrocenylsilane) **8** was found to be insoluble in organic solvents and this material was characterized by elemental analysis and derivatization. Substitution of the chlorine side groups in polymer **7** was achieved under mild conditions via reaction with the organolithium reagents MeLi, PhLi, and $LiC\equiv C(CH_2)_4H$ to afford the known polymers $[Fe(\eta\text{-}C_5H_4)_2SiMe_2]_n$ (**2a**) and $[Fe(\eta\text{-}C_5H_4)_2SiMePh]_n$ (**2d**) and the new polymer $[Fe(\eta\text{-}C_5H_4)_2\text{-}SiMeC\equiv C(CH_2)_4H]_n$ (**9**), respectively. The molecular weights for the completely halogen-substituted poly(ferrocenylsilanes) **2a**, **2d**, and **9** were estimated by gel permeation chromatography in THF to be in the range of $M_w = 7.4 \times 10^4$ to 1.7×10^5 and $M_n = 3.6 \times 10^4$ to 1.1×10^5 versus polystyrene standards. Substitution of the chlorine atoms in **8** was also demonstrated by reaction of the polymer with MeLi to give **2a**.

Introduction

Transition-metal-based polymers are attracting considerable attention as materials with new and potentially useful properties.[1,2] Ideally, the novel physical characteristics of transition metals and polymers might be combined into a single, processable material.[1] Ferrocene represents a particularly attractive component for incorporation into polymer structures because of its interesting physical and chemical properties and also its robust nature and low cost relative to other transition metal building blocks.[2]

Poly(ferrocenylsilanes) possess a backbone which consists of alternating ferrocene and organosilane groups and were first prepared as low molecular weight (M_w <7000), partially characterized materials in the late 1960's by the polycondensation reactions of $Fe(\eta\text{-}C_5H_4\text{-}Li)_2 \cdot TMEDA$ with organodichlorosilanes, $RR'SiCl_2$.[3] In 1992, we reported an alternative, chain growth route to high molecular weight ($M_w = 10^5–10^6$) poly(ferrocenylsilanes) **2** which involved the thermal ring-opening polymerization (ROP) of strained, silicon-bridged [1]-ferrocenophanes **1**.[4] Subsequent studies of the high molecular weight poly(ferrocenylsilanes) prepared via

[⊗] Abstract published in *Advance ACS Abstracts,* February 15, 1996.
(1) For example, see: (a) Pittman, C. U., Jr.; Carraher, C. E., Jr.; Reynolds, J. R. In *Encyclopedia of Polymer Science and Engineering*; Mark, H. F., Bikales, N. M., Overberger, C. G., Menges, G., Eds.; Wiley: New York, 1989; Vol. 10, p 541. (b) Sheats, J. E.; Carraher, C. E., Jr.; Pittman, C. U. *Metal-Containing Polymer Systems*; Plenum: New York, 1985. (c) Chisholm, M. H. *Angew. Chem., Int. Ed. Engl.* **1991**, *30*, 673. (d) Manners, I. *Chem. Br.* **1996**, *32*, 46.
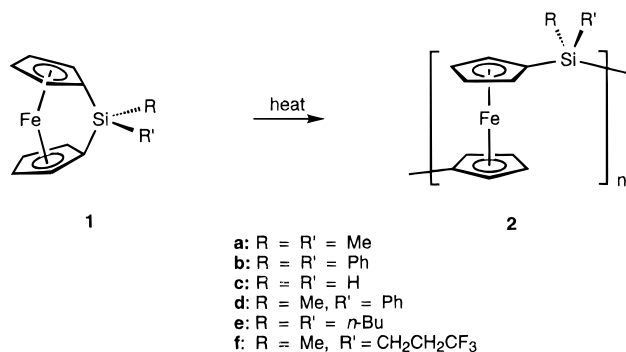
(2) For example, see: (a) Compton, D. L.; Rauchfuss, T. B. *Organometallics* **1994**, *13*, 4367. (b) Brandt, P. F.; Rauchfuss, T. B. *J. Am. Chem. Soc.* **1992**, *114*, 1926. (c) Nugent, H. M.; Rosenblum, M.; Klemarczyk, P. *J. Am. Chem. Soc.* **1993**, *115*, 3848. (d) Bayer, R.; Pöhlmann, T.; Nuyken, O. *Makromol. Chem. Rapid. Commun.* **1993**, *14*, 359. (e) Manners, I. *Adv. Mater.* **1994**, *6*, 68. (f) Gonsalves, K.; Zhan-ru, L.; Rausch, M. D. *J. Am. Chem. Soc.* **1984**, *106*, 3862. (g) Neuse, E. W.; Bednarik, L. *Macromolecules* **1979**, *12*, 187. (h) Patterson, W. J.; McManus, S.; Pittman, C. U. *J. Polym. Sci. A* **1974**, *12*, 837. (i) Altmann, M.; Bunz, U. H. F. *Angew. Chem., Int. Ed. Engl.* **1995**, *34*, 569. (j) Fyfe, H. B.; Mlekuz, M.; Zargarian, D.; Taylor, N. J.; Marder, T. B. *J. Chem. Soc., Chem. Commun.* **1991**, 188. (k) Khan, M. S.; Kakkar, A. K.; Ingham, S. L.; Raithby, P. R.; Lewis, J.; Spencer, B.; Wittmann, F.; Friend, R. H. *J. Organomet. Chem.* **1994**, *472*, 247. (l) Hagihara, N.; Sonogashira, K.; Takahashi, S. *Adv. Polym. Sci.* **1981**, *41*, 149.

(3) Rosenberg, H. U.S. Patent 3,426,053, 1969.
(4) Foucher, D. A.; Tang, B.-Z.; Manners, I. *J. Am. Chem. Soc.* **1992**, *114*, 6246.

a: R = R' = Me
b: R = R' = Ph
c: R = R' = H
d: R = Me, R' = Ph
e: R = R' = *n*-Bu
f: R = Me, R' = CH$_2$CH$_2$CF$_3$

thermal ROP have revealed that these materials possess a variety of interesting chemical and physical properties.[5–11] Recent studies of thermal ROP of silicon-bridged [1]ferrocenophanes with methylated cyclopentadienyl rings have indicated that the polymerization probably proceeds via initial heterolytic Si–C$_{ipso}$ bond cleavage.[12]

Our group has also recently reported alternative methods for inducing the ROP of silicon-bridged [1]-ferrocenophanes.[13] For example, in the presence of organolithium reagents, anionic ROP of **1a** is possible and living polymers can be formed.[8,14] Living anionic ROP provides access to transition-metal-based polymers with controlled architectures such as novel block copolymers.[14] Transition-metal-catalyzed ROP of **1a** to yield high molecular weight **2a** in solution at room temperature has also been reported.[15,16]

As in the case of all-organic analogs, modification of the structure and composition of transition-metal-based polymers offers considerable control of polymer properties. In this regard, we have approached the control of poly(ferrocenylsilane) properties by manipulating the substituents at silicon.[5,7] A particularly attractive method for controlling the structure of poly(ferrocenylsilanes) would be to use macromolecular substitution reactions on polymers which possess Si–Cl bonds.[17,18]

This might permit the introduction of side group substituents which are inconvenient or impossible to introduce directly via ROP methods. In this paper we report on our studies of the ROP of silicon-bridged [1]ferrocenophanes with chlorine substituents at silicon and the substitution chemistry of the resulting macromolecules.

Results and Discussion

A silicon-bridged[1]ferrocenophane (**4**) with two chlorine substituents at silicon was prepared in 1978 by
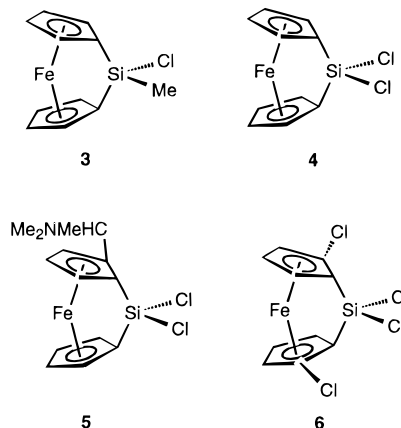
Wrighton from the reaction of Fe(η-C$_5$H$_4$Li)$_2$·TMEDA with SiCl$_4$.[19] Similar routes were used by Cullen[20] and Osborne[21] to prepare the alkylamino derivative, **5**, and the tetrachloro species, **6**, respectively. These highly moisture-sensitive compounds have been utilized as derivatizing agents for Pt and Au electrode surfaces. While the ring opening of **4** with traces of water on the electrode surfaces was suspected by Wrighton,[19] the ROP behavior of this species was not explored.

Synthesis of the Silicon-Bridged [1]Ferrocenophanes with Chlorine Substituents at Silicon. The silicon-bridged [1]ferrocenophanes **3** with methyl and chlorine substituents at silicon and **4** with two chlorine substituents at silicon were prepared by reactions of Fe(η-C$_5$H$_4$Li)$_2$·TMEDA with MeSiCl$_3$ and SiCl$_4$, respectively, at −78 °C in ether. These ferrocenophanes

3: R = Me   **7:** R = Me
4: R = Cl   **8:** R = Cl
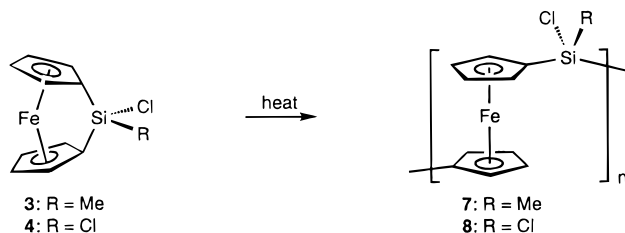
were obtained in high yield (80–90%) as moisture-sensitive, red crystalline solids by either vacuum sublimation or recrystallization (hexanes, −30 °C) of the

(5) Foucher, D. A.; Ziembinski, R.; Tang, B.-Z.; Macdonald, P. M.; Massey, J.; Jaeger, C. R.; Vancso, G. J.; Manners, I. *Macromolecules* **1993**, *26*, 2878.

(6) Foucher, D. A.; Honeyman, C. H.; Nelson, J. M.; Tang, B.-Z.; Manners, I. *Angew. Chem., Int. Ed. Engl.* **1993**, *32*, 1709.

(7) Foucher, D.; Ziembinski, R.; Petersen, R.; Pudelski, J.; Edwards, M.; Ni, Y.; Massey, J.; Jaeger, C. R.; Vancso, G. J.; Manners, I. *Macromolecules* **1994**, *27*, 3992.

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(11) For the work of other groups on poly(ferrocenylsilanes) and related materials, see: (a) Tanaka, M.; Hayashi, T. *Bull. Chem. Soc. Jpn.* **1993**, *66*, 334. (b) Nguyen, M. T.; Diaz, A. F.; Dement'ev, V. V.; Pannell, K. H. *Chem. Mater.* **1993**, *5*, 1389. (c) Hmyene, M.; Yassar, A.; Escorne, M.; Percheron-Guegan, A.; Garnier, F. *Adv. Mater.* **1994**, *5*, 564.

(12) Pudelski, J. K.; Manners, I. *J. Am. Chem. Soc.* **1995**, *117*, 7265.

(13) We have also reported the ROP of other [1]- and [2]metallocenophanes. See for example: (a) Reference 10. (b) Pudelski, J. K.; Gates, D. P.; Rulkens, R.; Lough, A.; Manners, I. *Angew. Chem., Int. Ed. Engl.* **1995**, *34*, 1506 and references cited therein.

(14) (a) Rulkens, R.; Ni, Y.; Manners, I. *J. Am. Chem. Soc.* **1994**, *116*, 12121. (b) Ni, Y.; Rulkens, R.; Manners, I. *J. Am. Chem. Soc.* **1996**, *118*, in press.

(15) Ni, Y.; Rulkens, R.; Pudelski, J. K.; Manners, I. *Macromol. Rapid Commun.* **1995**, *16*, 637.

(16) Tanaka, M.; Reddy, N. P.; Yamashita, H. *J. Chem. Soc., Chem. Commun.* **1995**, 2263.

(17) Macromolecular substitutions have been used extensively to control the properties of polyphosphazenes. See: (a) Allcock, H. R. *Chem. Eng. News* **1985**, *63* (11), 22. (b) Allcock, H. R. *J. Inorg. Organomet. Polym.* **1992**, *2*, 197.

(18) Macromolecular substitution reactions have recently been reported for polycarbosilanes; see: (a) Rushkin, I. L.; Interrante, L. V. *Macromolecules* **1995**, *28*, 5160. (b) Cummings, S.; Smith, D.; Wagener, K.; Miller, R.; Ginsburg, E. *Polym. Prepr. (Am. Chem. Soc., Div. Polym. Chem.)* **1995**, *36* (1), 697.

(19) Wrighton, M. S.; Palazzatto, M. C.; Bocarsly, A. B.; Bolts, J. M.; Fischer, A. B.; Nadjo, L. *J. Am. Chem. Soc.* **1978**, *100*, 7264.

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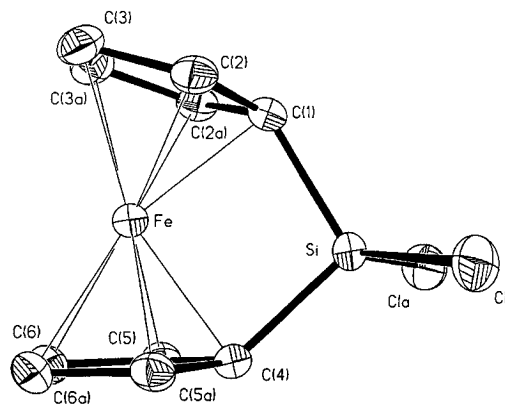
Figure 1. Molecular structure of **4** (with thermal ellipsoids drawn at the 50% probability level).

crude products. The chlorinated monomers were characterized by ^{29}Si, ^{13}C, and ^{1}H NMR spectroscopy. The ^{29}Si NMR spectra of both **3** and **4** (in C_6D_6) revealed sharp singlet resonances at 5.75 and −4.8 ppm, respectively. The most distinguishing feature of ^{13}C NMR (C_6D_6) spectra for most [1]ferrocenophanes is the upfield chemical shift of the ipso carbons attached to the bridging atom. For compounds **3** and **4** the ipso carbon chemical shifts are located at 33.8 and 36.1 ppm.[22] The ^{13}C and ^{1}H NMR spectra for **3** show unique resonances for the α and β hydrogens and carbon atoms of the cyclopentadienyl ring, which is a consequence of a lowered structural symmetry in comparison to **4**. Similar chemical shift patterns have been observed for other unsymmetrically substituted silicon-bridged [1]ferrocenophanes.[7] The ^{1}H NMR chemical shift values for **4** were found to be in good agreement with those previously reported.[19]

Crystal Structure of 4. In order to expand the database of structures of [1]ferrocenophanes, compound **4** was characterized by single-crystal X-ray diffraction. Dark red crystals of **4** suitable for an X-ray diffraction study were obtained from a high vacuum sublimation of the crude material (80 °C, 0.05 mmHg). A view of the molecular structure of **4** is shown in Figure 1. A summary of cell constants and data collection parameters is included in Table 1, and the fractional coordinates and important bond lengths and angles for **4** are listed in Tables 2 and 3. Comparative data for the present structure and other reported silicon-bridged [1]ferrocenophanes are tabulated in Table 4.

One other dichloro silicon-bridged [1]ferrocenophane, the alkylamino substituted dichloro species (**5**), has also been structurally characterized.[20] The structure of **4** reveals a number of similarities to that of **5** and also some subtle differences. Compounds **4** and **5** possess comparable ring-tilt angles, α (19.2 (4)° for **4** and 19.0(2)° for **5**), and the Fe−Si distance in **4** (2.588(1) Å) is only slightly shorter than in **5** (2.593(1) Å). The average Cp$_{ipso}$−Si bond lengths in each structure are nearly identical (within esd's) (Cp$_{ipso}$−Si: **4**, 1.848(4) Å; and **5**, 1.850(3) Å) as are the Cp$_{ipso}$−Si−Cp$_{ipso}$ bond angles (θ: **4**, 100.9(2)°; **5**, 100.7(1)°). A significantly larger difference is observed for the Cl−Si−Cl bond angle with a value of 111.1(1)° for **4** compared to a value of 107.3(1)° in **5**. The other structural features listed in Table 4 for **4** and **5** are also virtually identical. It is

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

Table 1. Summary of Crystal Data and Intensity Collection Parameters for 4

empirical formula	$C_{10}H_8Cl_2FeSi$
M_r	283.0
cryst class	monoclinic
space group	$C2/m$
a, Å	12.623(2)
b, Å	11.311(2)
c, Å	7.628(2)
β, deg	104.71(2)
V, Å^3	1053.5(8)
Z	4
D_{calc}, g cm^{-3}	1.784
μ(Mo Kα), cm^{-1}	20.0
$F(000)$	568
ω-scan width, deg	$0.60 + 0.35 \tan \theta$
range θ collcd, deg	2.5−27.0
tot. no. of rflns	1303
no. of unique rflns	1203
R_{int}	0.076
no. of obsd data used [$I > 3\sigma(I)$]	1030
R, %	2.69
R_w, %	2.94
GOF	1.11
$(\Delta/\sigma)_{max}$ in last cycle	0.00
no. of params refined	86
$\Delta\rho$ in final ΔF map, e Å^{-3}	0.28

Table 2. Final Fractional Coordinates and Thermal Parameters (Å^2) for the Non-Hydrogen Atoms of 4

atom	x	y	z	U_{eq}^a Å^2
Fe	0.805 77(4)	0.000 00	0.082 63(7)	0.0323(2)
Si	0.661 50(9)	0.000 00	0.270 52(14)	0.0368(3)
Cl	0.597 08(8)	0.148 42(9)	0.354 34(12)	0.0651(3)
C(1)	0.812 75(32)	0.000 00	0.348 44(48)	0.0360(12)
C(2)	0.870 35(24)	0.101 41(26)	0.303 71(38)	0.0421(9)
C(3)	0.956 59(24)	0.062 60(31)	0.231 96(43)	0.0521(11)
C(4)	0.641 83(30)	0.000 00	0.022 32(51)	0.0359(12)
C(5)	0.679 87(24)	−0.100 87(27)	−0.058 36(38)	0.0418(9)
C(6)	0.740 55(26)	−0.062 29(31)	−0.179 18(39)	0.0499(11)

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

Table 3. Selected Distances (Å) and Angles (deg) for 4 (Estimated Standard Deviations (Esd's) in Parentheses)

Distances			
Fe−Si	2.588(1)	Si−C(1)	1.850(4)
Fe−C(1)	2.007(4)	Si−C(4)	1.846(4)
Fe−C(2)	2.031(3)	C(1)−C(2)	1.445(4)
Fe−C(2a)	2.031(3)	C(1)−C(2a)	1.445(4)
Fe−C(3)	2.079(3)	C(2)−C(3)	1.407(5)
Fe−C(5)	2.029(3)	C(3)−C(3a)	1.416(7)
Fe−C(5a)	2.029(3)	C(4)−C(5)	1.436(4)
Fe−C(6)	2.080(3)	C(4)−C(5a)	1.436(4)
Fe−C(6a)	2.080(3)	C(5)−C(6)	1.409(5)
Si−Cl	2.038(1)	C(6)−C(6a)	1.409(7)
Si−Cla	2.038(1)		

Angles			
C(1)−Si−C(4)	100.9(2)	Cl−Si−Cla	111.1(1)
C(1)−Si−Cl	111.1(1)	Si−C(1)−C(2)	117.7(2)
C(1)−Si−Cla	110.9(1)	Si−C(1)−C(2a)	117.7(2)
C(4)−Si−Cl	111.2(1)	Si−C(4)−C(5)	117.9(2)
C(4)−Si−Cla	111.2(1)	Si−C(4)−C(5a)	117.9(2)

interesting to note that the presence of a strong electron-donating substituent on one of the cyclopentadienyl rings of **5** has very little effect on the structural features in comparison to **4**. With respect to the other silicon-bridged [1]ferrocenophanes **1a**−**c** listed in Table 4, the most notable change is in the Fe−Si distance. The relatively short Fe−Si distance in silicon-bridged [1]-ferrocenophanes (see Table 4) has previously been invoked as evidence for a weak dative Fe−Si bonding interaction in these species.[23] Particularly short Fe−

Table 4. Comparison of Important Structural Features of Selected Silicon-Bridged [1]Ferrocenophanes

	1a	1b	1c	4	5
Fe−X dist, Å	2.690(3)	2.636(5)	2.6729(6)	2.588(1)	2.593(1)
Fe displacement,[a] Å	0.2164(11)	0.183(12)	0.205(2)	0.194(4)	0.196(4)
ring tilt, α, deg	20.8(5)	19.1(10)	19.1(1)	19.2(4)	19.0(2)
β,[b] deg	37.0(6)	40.0(9)	39.1, 38.1(1)	40.7(5)	40.96(2)
C1−X−C6, θ, deg	95.7(4)	99.2(5)	97.21(7)	100.9(2)	100.70(14)
Cp−Fe−Cp, δ, deg	164.74(8)	167.3(6)	165.6(1)	166.5(2)	166.3(1)
ref	33	34	28	this work	20

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

Si distances in both **4** and **5** compared to methyl- (**1a**) and phenyl- (**1b**) substituted silicon-bridged [1]ferrocenophanes could possibly be related to the electron-withdrawing effect of the chlorine substituents. The Fe−Si distance in **1b** is intermediate between that in **1a** and **4** and follows from the inductive effect of the phenyl groups relative to methyl and chlorine substituents (**4**, Fe−Si, 2.588(1) Å < **1b**, Fe−Si, 2.636(5) Å < **1a**, Fe−Si, 2.690(3) Å).

Thermal ROP of 3 and 4. Characterization of Poly(ferrocenylsilanes) 7 and 8. In order to determine whether compounds **3** and **4** would undergo thermal ROP, preliminary investigations were carried out using DSC. Milligram samples of both **3** and **4** were hermetically sealed in DSC pans under nitrogen and were then heated to 280 °C. In both instances, no melting transitions were observed and only at between 240−250 °C was a ROP exotherm detected. When a preparative scale sample of **3** was heated at 250 °C for 25 min in a sealed evacuated Pyrex tube, the poly-(ferrocenylsilane) **7** was formed. This material dissolved completely, albeit slowly, in THF and CH_2Cl_2. Dissolution of crude **7** in THF followed by precipitation of the resulting solution into dry hexanes afforded analytically pure material as a fibrous, orange solid in 83% yield. Analysis of **7** by GPC could not be undertaken due to the hydrolytic sensitivity of the Si−Cl bonds. Evidence for successful thermal ROP was nevertheless provided by NMR. For example, the ^{13}C NMR chemical shift of the *ipso* cyclopentadienyl carbon changed from a high-field value (33.8 ppm) typical of a strained, ring-tilted [1]ferrocenophane in the spectrum of **3** to a value (70.0 ppm) characteristic of an unstrained ferrocene derivative in the spectrum of **7**.[22] Interestingly, three ^{29}Si NMR resonances at 16.86, 16.81, and 16.75 ppm were observed for **7**, in an approximate 1:2:1 ratio (see Figure 2). The appearance of three peaks is suggestive of an atactic polymer with resolution of the triad structure.[24] Thus the triad configurations in polymer **7** (Figure 3) would involve four distinct tacticity environments composed of two successive dyads, namely *mm*, *mr*, *rm*, and *rr*, where *m* and *r* are meso (adjacent units of the same configuration) and racemic (adjacent units of opposite configuration) forms. Since *mr* and *rm* configurations are mirror images, they are indistinguishable by NMR and give rise to the expected statistical distribution of 1:2:1 in the ^{29}Si NMR spectrum. It is surprising that the atacticity detected by ^{29}Si NMR is not also apparent in the ^{13}C NMR spectra, but this is probably a consequence of the higher sensitivity of ^{29}Si NMR to structural differences.[25]
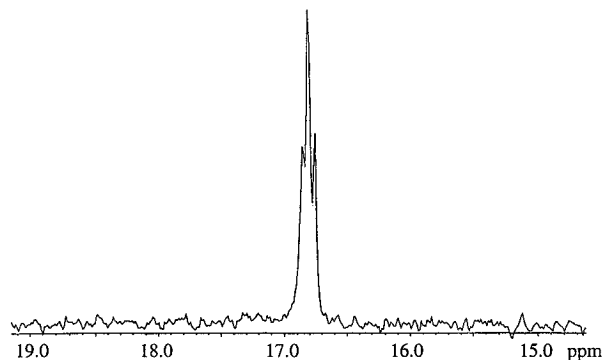
Figure 2. ^{29}Si NMR of **7**, showing the expected statistical 1:2:1 distribution of triads for an atactic polymer.
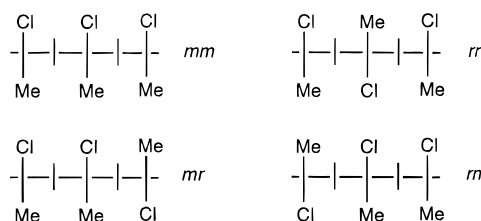
Figure 3. Triad configurations in polymer **7**.

Similar thermal treatment of **4** at 250 °C afforded a completely THF-insoluble, moisture-sensitive red solid. This material was identified as **8** on the basis of elemental analysis and derivatization (see below).

It was noteworthy that both **3** and **4** undergo thermal ROP at temperatures (*ca.* 250 °C) significantly higher than for dialkyl-substituted analogues such as **1a**, which polymerize at 130−150 °C.[4,10] We have recently noted that an increase in methylation of the cyclopentadienyl ligands also leads to an increase in the temperature required for thermal ROP.[26] Both of these sets of observations are consistent with a heterolytic cyclopentadienyl carbon−silicon bond cleavage mechanism which involves a buildup of negative charge at the cyclopentadienyl carbon and positive charge at silicon,[12] which is analogous to the proposed mechanism for the thermal ROP of cyclic carbosilanes.[27]

Previous work has shown that poly(ferrocenylsilanes) exhibit glass transitions with small changes in heat capacity which are readily observable by DSC.[10] Additionally, symmetrically substituted species (e.g. **2e**)

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(24) Heatley, F. In *NMR Spectroscopy of Polymers*; Ibbett, R. N., Ed.; Blackie Academic & Professional: London, 1993; pp 1−49.
(25) Unsymmetrically substituted poly(ferrocenylmethylsilanes) possess ^{29}Si NMR chemical shifts which range from −3.4 to −20.0 ppm. However, the ^{13}C NMR shifts for the Si−Me groups range only from −1.5 to −5.6 ppm. See ref 7.
(26) Pudelski, J. K.; Foucher, D. A.; Honeyman, C. H.; Macdonald, P. M.; Manners, I.; Barlow, S.; O'Hare, D. *Macromolecules* **1996**, *29*, 1894.
(27) See, for example: (a) Salamone, J. C.; Fitch, W. L.; Ashe, A. J. *J. Polym. Sci. (A-1)* **1971**, *9*, 1741. (b) Kriner, W. A. *J. Polym. Sci. (A-1)* **1966**, *4*, 444.

possess the ability to crystallize in some cases[10,28] and show melt transitions by DSC analysis. In order to examine the conformational flexibility and morphology of chlorine-substituted poly(ferrocenylsilanes), the thermal transition behavior of **7** and **8** was investigated. DSC analysis of **7** showed a T_g at 59 °C, identical to that previously obtained for **2f**.[7] No melting transition was observed for this polymer, which is typical for most unsymmetrically substituted poly(ferrocenylsilanes). Analysis of **8** by DSC revealed a T_g at 29 °C, which is similar to that reported for **2a** (33 °C).[5] A weak endothermic transition at 156 °C and a strong endothermic transition at 185 °C were also observed and were assigned to melt transitions for this species. This behavior is similar to that detected for **2e**.[29]

Substitution Reactions of 7 and 8 with Organolithium Reagents. We probed the substitutional lability of **7** by reacting this material with a slight excess of the organolithium reagents MeLi, PhLi, and LiC≡C-(CH$_2$)$_4$H in THF. These were selected as representative examples with sp^3-, sp^2-, and sp-hybridized nucleophilic carbon centers, respectively. In all cases, complete substitution was effected simply by stirring at 25 °C for 24 h. The resulting substitution products, **2a,d** and **9**,

7

2a: R = Me
2d: R = Ph
9: R = C≡C(CH$_2$)$_4$H
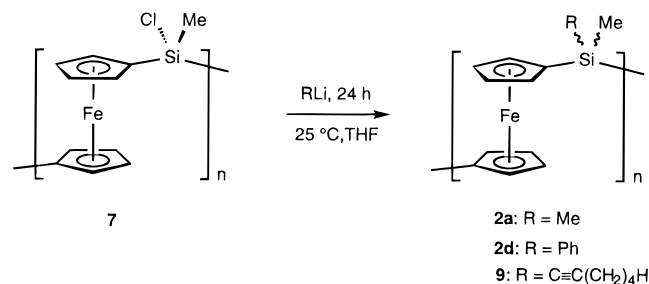
were all moisture-stable materials which were isolated in moderate to high yield (63–90%) by concentration of the reaction mixture, precipitation by addition to methanol, and filtration. Similarly, when solid **8** was stirred in THF and reacted with MeLi for 24 h, complete substitution of the Cl atoms for methyl groups was observed. The resulting polymer **2a** was purified by a method similar to that used for the products of the substitution reactions with **7**. The complete conversion to the substituted derivatives was confirmed by ^{1}H NMR and also by ^{29}Si NMR, a highly sensitive probe of poly-(ferrocenylsilane) microstructure.

Analysis of **2a,d** and **9** by GPC in THF vs polystyrene standards indicated that these materials possessed molecular weights in the range $M_w = (1.3–1.4) \times 10^5$ and $M_n = (5.0–6.4) \times 10^4$ with polydispersities of 2.2–2.7. As **2a,d** and **9** were all prepared from the same batch of the precursor **7**, the GPC data for these substituted derivatives provide an estimate of the molecular weight and polydispersity of **7**. Analysis of the polymer **2a** derived from **8** revealed a slightly lower molecular weight of $M_w = 7.4 \times 10^4$ and $M_n = 3.6 \times 10^4$. DSC analysis of **9** revealed a T_g at 21 °C, which falls below that reported for **2** (R = Me, R′ = CH=CH$_2$) (28 °C) and is higher than those reported for unsymmetrically substituted poly(ferrocenylsilanes) with one

methyl substitutent and one long-chain hydrocarbon substituent such as n-C$_{18}$H$_{37}$ (1 °C).[7]

A clear advantage of the macromolecular substitution route to poly(ferrocenylsilanes) is illustrated by the synthesis of **9**. Since (1-hexynyl)methyldichlorosilane is neither commercially available nor convenient to synthesize, access to **9** via preparation and thermal ROP of the hexynyl-substituted silicon-bridged [1]ferrocenophane would clearly be less straightforward than the macromolecular substitution route. It is also important to note that access to substituted poly(ferrocenylsilanes) via substitution reactions of chlorinated monomers **3** and **4** followed by thermal ROP is probably difficult since strained silicon-bridged [1]ferrocenophanes undergo facile ring-opening reactions in the presence of small quantities of organolithium reagents.[8,14]

Transition-Metal-Catalyzed Polymerizations of 3 and 4. Previous work has shown that the silicon-bridged [1]ferrocenophane **1a**, in a similar manner to cyclic carbosilanes,[30] will undergo ROP to yield high molecular weight polymer in the presence of a variety of metal catalysts.[15,16] It therefore was of interest to investigate whether transition-metal-catalyzed ROP of **3** and **4** would also be possible. Indeed, we found that reactions of **3** with small quantities of PtCl$_2$, Pt(1,5-cyclooctadiene)$_2$, and Pd(1,5-cyclooctadiene)Cl$_2$ in benzene afforded the polymer **7** in all cases, as shown by ^{1}H and ^{29}Si NMR.

Reaction of the polymer samples formed via the transition-metal-catalyzed ROP of **3** with a slight excess of MeLi in benzene over 24 h followed by precipitation into hexanes, filtration, and drying afforded polymer **2a**. Analysis of the polymer sample produced using PtCl$_2$ as a catalyst by GPC in THF vs polystyrene standards showed that this material possessed a substantially higher molecular weight ($M_w = 1.7 \times 10^5$, $M_n = 1.1 \times 10^5$, PDI = 1.5) than those samples produced with the other two catalysts ($M_w = 3.2 \times 10^3$–1.1×10^4, $M_n = 2.2 \times 10^3$–7.8×10^3, PDI = 1.4–1.5). As these samples were all produced from the same batch of the precursor **3**, the GPC data provides information on the relative effectiveness of the different catalysts.

A silicon-bridged [1,1′]ferrocenophane was previously identified as a byproduct of the ROP reaction of **1a** using Pd(1,5-cyclooctadiene)Cl$_2$ as catalyst.[15,31] Interestingly, when this catalyst was used for the polymerization of **3**, besides resonances for residual monomer **3** and polymer **7**, two additional resonances at 16.5 and 17.4 ppm of equal intensity were observed by ^{29}Si NMR. We tentatively attribute these peaks to the *cis* and *trans* isomers **10** and **11**, analogues of the *cis* and *trans* isomers of 1,4-disubstituted cyclohexanes.

Summary

We have synthesized the first examples of poly-(ferrocenylsilanes) with halogen substituents attached to the skeletal silicon atoms. The presence of Si–Cl bonds was not found to dramatically influence the

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10 trans   **11** cis
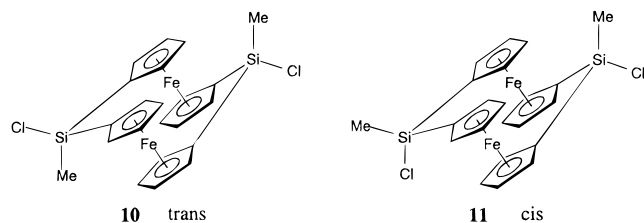
ability of the [1]ferrocenophane precursors to polymerize via either thermally-induced or transition-metal-catalyzed ROP. However, the higher temperature required for the thermal ROP of **3** and **4** compared to the dialkyl-substituted analogs such as **1a** is consistent with the previously proposed heterolytic cyclopentadienyl carbon–silicon bond cleavage mechanism for initiation, where negative charge builds up on carbon and a positive charge on silicon.[12] The substitutionally labile chlorine substituents of **7** and **8** were successfully replaced by organic substituents via reaction with organolithium reagents. This type of substitution process is likely to be a useful method for the preparation of functionalized poly(ferrocenylsilanes). Further work aimed at exploring the synthetic scope of this methodology is in progress and will be reported in the near future.

Experimental Section

Trichloromethylsilane, tetrachlorosilane, methyllithium, phenyllithium, 1-hexyne, cyclooctadiene, $PtCl_2$, and $PdCl_2$ were purchased from Aldrich. Dilithioferrocene·TMEDA was synthesized as described in the literature.[32] All reactions and manipulations were carried out under an atmosphere of prepurified nitrogen using either Schlenk techniques or an inert-atmosphere glovebox (Vacuum Atmospheres, Innovative Technologies Inc.). NMR spectra were recorded on either Varian Gemini 200 or Varian XL 400 instruments. ^1H NMR spectra were referenced to residual protonated C_6D_6 at 7.15 ppm, and ^{13}C spectra were referenced to the C_6D_6 signal at 128.0 ppm. ^{29}Si NMR spectra were recorded utilizing normal (proton coupled) or DEPT (proton decoupled, $J_{Si-H} = 6.7$ Hz) pulse sequences and were referenced externally to TMS. IR spectra were recorded on a Nicolet Magna 550 IR spectrometer. Mass spectra were obtained with a VG 70−250S mass spectrometer operating in electron impact mode. DSC analyses were performed at a heating/cooling rate of 10 °C·min^{-1} under prepurified N_2 using a Perkin-Elmer DSC 7 differential scanning calorimeter. Molecular weight estimates were made via gel permeation chromatography using a Waters Associates liquid chromatograph equipped with a 510 HPLC pump, U6K injector, ultrastyragel gel columns with a pore size between 10^3 and 10^5 Å, and a Waters 410 differential refractometer. A flow rate of 1.0 mL/min was used, and samples were dissolved in THF containing 0.1% tetra-*n*-butylammonium bromide. Polystyrene standards were used for calibration purposes. Elemental analyses were performed by Quantitative Technologies Inc., Whitehouse, NJ.

Synthesis of Fe(η-C_5H_4)$_2$SiMeCl (3). A slurry of Fe(η-C_5H_4Li)$_2$·TMEDA (10.5 g, 33.4 mmol) in 150 mL of dry ether was cooled to −78 °C and treated dropwise with 4.3 mL (5.48 g, 36.7 mmol) of freshly distilled MeSiCl$_3$. The resulting mixture was allowed to warm to RT (room temperature) and stirred overnight. Ether and excess MeSiCl$_3$ were removed in vacuo and the crude product redissolved in 200 mL of dry

hexanes. The resulting slurry was filtered to remove LiCl and the filtrate concentrated in vacuo affording a red-orange residue. Vacuum sublimation of this residue (60 °C, 0.005 mmHg) afforded 7.71 g (88%) of **3** as a red-orange solid.

Data for **3**: ^1H NMR (200 MHz, C_6D_6) δ 4.35 (m, 2H, Cp), 4.29 (m, 2H, Cp), 4.22 (m, 2H, Cp), 3.70 (m, 2H, Cp), 0.52 (s, 3H, Me); ^{13}C NMR (50.3 MHz, C_6D_6) δ 78.8 (Cp), 78.4 (Cp), 76.1 (Cp), 73.9 (Cp), 33.8 (Cp–Si), 0.10 (Me); ^{29}Si NMR (79.5 MHz, C_6D_6) δ 5.75; HRMS (*m/e*) calcd for $C_{11}H_{11}ClFeSi$ 261.9668, found 261.9677. Anal. Calcd for $C_{11}H_{11}ClFeSi$: C, 50.31; H, 4.22. Found: C, 50.22; H, 4.20.

Fe(η-C_5H_4)$_2$SiCl$_2$ (4). This compound was prepared by the method of Wrighton et al.[19] Additional data: ^{13}C NMR (100.6 MHz, C_6D_6) δ 79.5 (Cp), 74.8 (Cp), 36.1 (Cp–Si); ^{29}Si NMR (79.5 MHz, C_6D_6) δ −4.8.

[Fe(η-C_5H_4)$_2$SiMeCl]$_n$ (7). A Pyrex tube was charged with 0.30 g of **3** and then flame sealed under vacuum (0.005 mmHg). The tube was then heated at 250 °C for 25 min. The sample melted, increased in viscosity, and became immobile after 10 min. The tube was cooled and broken open, and the contents were dissolved in 3 mL of dry THF. The addition of dry hexanes (300 mL) resulted in the precipitation of an amber solid. Filtration followed by drying in vacuo afforded 0.25 g (83%) of **7** as an amber, fibrous solid.

Data for **7**: ^1H NMR (200 MHz, C_6D_6) δ 4.38 (br s, 4H, Cp), 4.32 (br s, 2H, Cp), 4.21 (br s, 1H, Cp), 4.17 (br s, 1H, Cp), 0.84 (br s, 3H, Me); ^{13}C NMR (100.6 MHz, C_6D_6) δ 74.4 (Cp), 74.3 (Cp), 73.4 (Cp), 73.3 (Cp), 70.0 (Cp–Si), 2.5 (Me); ^{29}Si NMR (79.5 MHz, C_6D_6) δ 16.86, 16.81, 16.75 (relative intensities 1:2:1). Anal. Calcd for $C_{11}H_{11}ClFeSi$: C, 50.31; H, 4.22; Cl, 13.50. Found: C, 50.42; H, 4.37; Cl, 13.38. DSC: $T_g = 59$ °C.

[Fe(η-C_5H_4)$_2$SiCl$_2$]$_n$ (8). A Pyrex tube was charged with 1.00 g (3.5 mmol) of **4** and then flame sealed under vacuum (0.005 mmHg) and heated at 250 °C for 25 min. The sample melted, increased in viscosity, and became immobile after 8 min. The tube was cooled and broken open, yielding a quantitative amount of an insoluble dark red material.

Data for **8**: Anal. Calcd for $C_{10}H_8Cl_2FeSi$: C, 42.44; H, 2.85; Cl, 25.05. Found: C, 42.43; H, 2.97; Cl, 24.69. DSC: $T_g = 29$ °C, $T_m = 156, 185$ °C.

Substitution Reactions of 7. With MeLi To Yield 2a. A solution of **7** in 125 mL of THF (0.25 g, 0.95 mmol of Si−Cl) was cooled to −20 °C and treated with a 1.1 M ethereal solution of MeLi (1.1 mL, 1.2 mmol). The resulting mixture was allowed to warm to RT and stirred for 24 h. The resulting orange solution was quenched with methanol (1 mL of MeOH in 9 mL of THF), concentrated to ca. 5 mL, and then added dropwise to 500 mL of methanol. A fibrous amber solid precipitated and was collected by filtration, washed with 200 mL of methanol, and dried in vacuo to afford 0.20 g (87%) of **2a**.

^1H and ^{29}Si NMR data were identical to that of authentic **2a** prepared via TROP of **1a**: ^1H NMR (200 MHz, C_6D_6) δ 4.28 (br s, 4H, Cp), 4.11 (br s, 4H, Cp), 0.55 (br s, 6H, Me); ^{29}Si NMR (79.5 MHz, C_6D_6) δ −6.4; GPC $M_w = 1.4 \times 10^5$, $M_n = 6.4 \times 10^4$, PDI (M_w/M_n) = 2.2.

With PhLi To Yield 2d. A solution of **7** in 125 mL of THF (0.25 g, 0.95 mmol of Si−Cl) was cooled to −10 °C and treated with a 1.31 M solution of PhLi in cyclohexane/ether (7:3) (0.9 mL, 1.2 mmol). The mixture was allowed to warm to RT and stirred for 24 h. The resulting orange solution was quenched with methanol (1 mL of MeOH in 9 mL of THF), concentrated to ca. 5 mL, and then added dropwise to 500 mL of methanol. A fibrous orange solid precipitated and was collected by filtration, washed with 200 mL of methanol, and dried in vacuo to afford 0.18 g (63%) of **2d**.

^1H and ^{29}Si NMR data were identical to that of a sample of **2d** prepared via TROP of **1d**: ^1H NMR (200 MHz, C_6D_6) δ 7.72 (br m, 2H, *o*-Ph), 7.25 (br m, 3H, *m*- and *p*-Ph), 4.14−4.07 (br

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m, 8H, Cp), 0.75 (br s, 3H, Me); ^{29}Si NMR (79.5 MHz, C_6D_6) δ −10.9; GPC M_w = 1.4 × 10⁵, M_n = 5.2 × 10⁴, PDI (M_w/M_n) = 2.7.

With LiC≡C(CH_2)$_4$H) To Yield 9. A solution containing 0.4 mL of freshly distilled 1-hexyne (0.29 g, 3.5 mmol) and 7.5 mL of THF was cooled to −10 °C and treated with 1.1 mL of a 1.6 M hexanes solution of BuLi (1.7 mmol). The resulting mixture was allowed to warm to RT and stirred for 2 h, after which a cooled solution (−10 °C) containing **7** (0.22 g, 0.84 mmol of Si−Cl) in 75 mL of THF was added. The resulting mixture was allowed to warm to RT and stirred for 24 h. The amber solution was concentrated to ca. 5 mL and then added dropwise to 500 mL of methanol. A solid precipitated and was collected by filtration, washed with 200 mL of methanol, and dried in vacuo to afford 0.23 g (90%) of **9** as a yellow-orange fibrous solid.

Data for **9**: ^{1}H NMR (200 MHz, C_6D_6) δ 4.57 (br s, 4H, Cp), 4.49 (br s, 2H, Cp), 4.35 (br s, 2H, Cp), 2.2−2.1 (br m, 2H, C≡CCH_2), 1.6−1.4 (br m, 4H, C≡CCH$_2$CH_2CH_2−), 1.0−0.8 (br m, 6H, Si−CH_3, −CH$_2$CH_3); ^{13}C NMR (100.6 MHz, C_6D_6) δ 108.8 (SiC≡C−), 83.4 (SiC≡C−) 74.6 (Cp), 74.2 (Cp), 72.9 (Cp), 72.8 (Cp), 69.8 (Cp−Si), 31.2 (SiC≡CCH$_2$−), 22.4 (SiC≡CCH$_2$CH_2−), 20.0 (SiC≡CCH$_2$CH$_2$CH_2−), 13.9 (SiC≡C-CH$_2$CH$_2$CH$_2$CH_3), −0.14 (SiCH_3); ^{29}Si NMR (79.5 MHz, C_6D_6) δ −24.9; IR (NaCl) 2173 cm⁻¹ (C≡C stretch); GPC M_w = 1.3 × 10⁵, M_n = 5.0 × 10⁴, PDI (M_w/M_n) = 2.6. Anal. Calcd for $C_{17}H_{20}FeSi$: C, 66.23; H, 6.51. Found: C, 65.51; H, 6.60. DSC: T_g = 21 °C.

Substitution Reaction of 8 with MeLi To Yield 2a. Polymer **8** (0.63 g, 4.46 mmol of Si−Cl) was suspended in 250 mL of THF at 0 °C, and a 25% excess of a 1.4 M solution of MeLi in diethyl ether (5.0 mL, 7.0 mmol) was added. The resulting mixture was warmed to RT and stirred for 24 h, after which most of the solid had dissolved. The resulting orange solution was quenched with methanol (1 mL of MeOH in 9 mL of THF), concentrated to ca. 5 mL, and then added dropwise to 500 mL of methanol. A fibrous orange solid precipitated which was collected by filtration, washed with 200 mL of methanol, and dried in vacuo to afford 0.20 g (37%) of **2a** as an orange, fibrous solid.

^{1}H and ^{29}Si NMR data were identical to that of a sample of **2a** prepared via TROP of **1a**: ^{1}H NMR (200 MHz, C_6D_6) δ 4.28 (br s, 4H, Cp), 4.11 (br s, 4H, Cp), 0.55 (br s, 6H, Me); ^{29}Si NMR (79.5 MHz, C_6D_6) δ −6.4; GPC M_w = 7.4 × 10⁴ M_n = 3.6 × 10⁴, PDI (M_w/M_n) = 2.1.

Transition Metal-Catalyzed Polymerizations of 3. In a glovebox, three 0.10 g (0.38 mmol) samples of freshly prepared **3** were each dissolved in 3 mL of C_6D_6. To the individual samples was added approximately 0.02−0.05 equiv of catalyst: Sample A, $PtCl_2$; sample B, Pt(1,5-cyclooctadiene)$_2$; sample C, Pd(1,5-cyclooctadiene)Cl$_2$. The samples were stirred at 25 °C for 24 h, and the progress of polymerization monitored directly by ^{1}H and ^{29}Si NMR. Finally, the samples of **7** were converted to **2a** via reaction with a slight excess of MeLi as described above. Polymer **2a** was isolated by precipitation into hexanes and was characterized by NMR and GPC.

(A) With $PtCl_2$. Analysis of the polymerization mixture by ^{1}H NMR showed quantitative conversion of **3** after 24 h. The ^{1}H NMR and ^{29}Si NMR data obtained were in excellent agreement with that for **7** prepared by thermal ROP. The yield of polymer after conversion of **7** to **2a** and precipitation into hexanes was 0.079 g (86%). Data for **2a**: The ^{1}H NMR and ^{29}Si NMR were in agreement with that for **2a** prepared by thermal ROP. GPC: M_w = 1.7 × 10⁵, M_n = 1.1 × 10⁵, PDI =1.5.

(B) With Pt(1,5-cyclooctadiene)$_2$. Analysis of the polymerization mixture by ^{1}H NMR showed a 52% conversion of **3** after 24 h. The ^{1}H NMR and ^{29}Si NMR data were in agreement with that for **7** prepared by thermal ROP. The yield of polymer after conversion of **7** to **2a** and precipitation into hexanes was 0.045 g (49%). Data for **2a**: The ^{1}H NMR and ^{29}Si NMR were in agreement with that for **2a** prepared by thermal ROP. GPC: M_w = 3.2 × 10³, M_n = 2.2 × 10³, PDI = 1.5

(C) With Pd(1,5-cyclooctadiene)Cl$_2$. Analysis of the polymerization mixture by ^{1}H NMR showed a 70% conversion of **3** after 24 h. The ^{1}H NMR and ^{29}Si NMR data were in agreement with that for **7** prepared by thermal ROP, and in addition the ^{29}Si NMR showed resonances at 16.5 and 17.4 ppm which were tentatively assigned to **10** and **11**. The yield of polymer after conversion of **7** to **2a** and precipitation into hexanes was 0.042 g (46%). Data for **2a**: The ^{1}H NMR and ^{29}Si NMR spectra were in agreement with those for **2a** prepared by thermal ROP. GPC: M_w = 1.1 × 10⁴, M_n = 7.8 x10³, PDI = 1.4.

Supporting Information Available: Tables of complete bond lengths and angles, anisotropic thermal parameters, hydrogen atom coordinates and U values, and a figure showing the molecular structure of **4** (4 pages). Ordering information is given on any current masthead page.

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