

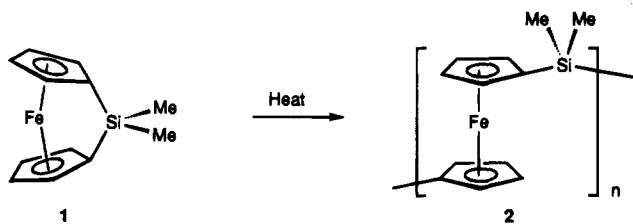
A Heterolytic Cyclopentadienyl Carbon–Silicon Bond Cleavage Mechanism for the Thermal Ring-Opening Polymerization of Silicon-Bridged [1]Ferrocenophanes

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Received November 8, 1994

High molecular weight polymers containing skeletal transition metal atoms are attracting increasing attention because of their interesting properties, but in general, synthetic routes to these materials are poorly developed.^{1,2} With this in mind, in 1992 we reported³ the discovery that strained, ring-tilted silicon-bridged [1]ferrocenophanes (e.g., **1**) undergo thermal ring-opening polymerization (TROP) to afford soluble, high molecular weight poly(ferrocenylsilanes) (e.g., **2**).^{3–6} We have



subsequently extended this TROP methodology to [1]ferrocenophanes containing germanium and phosphorus in the bridge, and also to hydrocarbon-bridged [2]metallocenophanes.^{6–8} Studies of the resulting transition metal-containing polymers have revealed that these materials possess a variety of interesting electrochemical, preceramic, morphological, and, when oxidized, magnetic properties.^{3–6,9–13}

(1) (a) Chisholm, M. H. *Angew. Chem., Int. Ed. Engl.* **1991**, *30*, 673. (b) Mark, J. E.; Allcock, H. R.; West, R. *Inorganic Polymers*; Prentice Hall: Englewood Cliffs, NJ, 1992. (c) Pittman, C. U.; Carraher, C. E.; Reynolds, J. R. In *Encyclopedia of Polymer Science and Engineering*; Mark, H. F., Bikales, N. M., Overberger, C. G., Eds.; Wiley: New York, 1987; Vol. 10, pp 541–594. (d) Allcock, H. R. *Adv. Mater.* **1994**, *6*, 106.

(2) For recent examples of transition metal-based polymeric materials, see: (a) Fyfe, H. B.; Mlekuz, M.; Zargarian, D.; Taylor, N. J.; Marder, T. B. *J. Chem. Soc., Chem. Commun.* **1991**, 188. (b) Tenhaeff, S. C.; Tyler, D. R. *Organometallics* **1992**, *11*, 1466. (c) Davies, S. J.; Johnson, B. F. G.; Khan, M. S.; Lewis, J. *J. Chem. Soc., Chem. Commun.* **1991**, 187. (d) Nugent, H. M.; Rosenblum, M.; Klemarczyk, P. *J. Am. Chem. Soc.* **1993**, *115*, 3848. (e) Dembek, A. A.; Fagan, P. J.; Marsi, M. *Macromolecules* **1993**, *26*, 2992. (f) Brandt, P. F.; Rauchfuss, T. B. *J. Am. Chem. Soc.* **1992**, *114*, 1926. (g) Roesky, H. W.; Lücke, M. *Angew. Chem., Int. Ed. Engl.* **1989**, *28*, 493. (h) Bayer, R.; Pöhlmann, T.; Nuyken, O. *Makromol. Chem., Rapid Commun.* **1993**, *14*, 359.

(3) Foucher, D. A.; Tang, B.-Z.; Manners, I. *J. Am. Chem. Soc.* **1992**, *114*, 6246.

(4) 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.

(5) 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.

(6) Manners, I. *Adv. Organomet. Chem.* **1995**, *37*, 131.

(7) Nelson, J. M.; Rengel, H.; Manners, I. *J. Am. Chem. Soc.* **1993**, *115*, 7035.

(8) Nelson, J. M.; Lough, A. J.; Manners, I. *Angew. Chem., Int. Ed. Engl.* **1994**, *33*, 989.

(9) For the work of other groups on poly(ferrocenylsilanes) and related materials, see: (a) Rosenberg, H. U.S. Patent 3,426,053, 1969. (b) Tanaka, M.; Hayashi, T. *Bull. Chem. Soc. Jpn.* **1993**, *66*, 334. (c) Nguyen, M. T.; Diaz, A. F.; Dement'ev, V. V.; Pannell, K. H. *Chem. Mater.* **1993**, *5*, 1389.

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

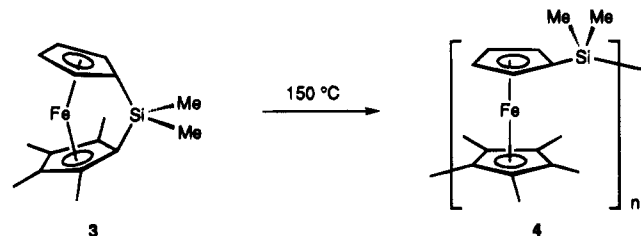
(11) Rulkens, R.; Lough, A. J.; Manners, I. *J. Am. Chem. Soc.* **1994**, *116*, 797.

(12) Tang, B.-Z.; Petersen, R.; Foucher, D. A.; Lough, A. J.; Coombs, N.; Sodhi, R.; Manners, I. *J. Chem. Soc., Chem. Commun.* **1993**, 523.

Although there has been considerable progress concerning the scope of the TROP route and the properties of the resulting polymeric materials, nothing has been reported regarding the mechanism of the polymerization reactions. In particular, the fundamental question of whether the TROP reactions proceed via cleavage of bonds between *ipso*-cyclopentadienyl (Cp) carbon atoms and bridging atoms or, alternatively, via cleavage of metal–Cp bonds remains unresolved. A report¹⁴ that reaction of ferrocene and 1,1'-dimethylferrocene at 250 °C affords a 60% yield of methylferrocene suggests that a M–Cp cleavage TROP mechanism cannot be ruled out, especially since M–Cp bonding (and bridge–Cp, also) is possibly weakened in strained metallocenophanes. Indeed, considering the case of silicon-bridged [1]ferrocenophanes, the Fe–Cp bond energy of ferrocene (220 kJ/mol) is considerably lower than the Si–C bond energy (318 kJ/mol).¹⁵ Furthermore, we have recently observed facile, thermally induced M–(π -hydrocarbon) bond cleavage in reactions of related silicon-bridged metallocenophanes.¹⁶ In this paper, we report the first mechanistic studies of these TROP reactions. In particular, we describe studies of the TROP of a silicon-bridged [1]ferrocenophane (**3**) with unsymmetrically methylated cyclopentadienyl rings, which was designed to allow us to distinguish between a Si–Cp and an Fe–Cp bond cleavage mechanism.¹⁷

We reasoned that if TROP of **3** proceeded through Si–Cp^H and Si–Cp^{Me} bond cleavage (Cp^H = C₅H₄, Cp^{Me} = C₅Me₄), then the resulting polymeric product **4** would contain three silicon environments (Cp^HSiCp^H, Cp^HSiCp^{Me}, and Cp^{Me}SiCp^{Me}) but only a single iron environment (Cp^HFeCp^{Me}). Conversely, if Fe–Cp^H and Fe–Cp^{Me} cleavage occurred, then **4** would contain a single silicon environment (Cp^HSiCp^{Me}) but three iron environments (Cp^HFeCp^H, Cp^HFeCp^{Me}, and Cp^{Me}FeCp^{Me}). We felt that the two cleavage possibilities would be unambiguously distinguished by using ¹H, ¹³C, and ²⁹Si NMR to probe the silicon environments of **4** and by using cyclic voltammetry to probe the iron environments of **4**.

TROP of **3** was smoothly effected by heating the compound in the melt at 150 °C in an evacuated, sealed Pyrex tube for 1 h. The resulting orange, fibrous poly(ferrocenylsilane) **4**, obtained in 63% yield, was completely soluble in THF and was found to be of high molecular weight ($M_w = 3.4 \times 10^5$, $M_n = 2.3 \times 10^5$).¹⁸



Analysis of the microstructure of **4** by ¹H NMR led to the detection of three broad resonances in the SiMe₂ region in a

(13) Hmyene, M.; Yasser, A.; Escorne, M.; Percheron-Guegan, A.; Garnier, F. *Adv. Mater.* **1994**, *6*, 564.

(14) Allcock, H. R.; McDonnell, G. S.; Riding, G. H.; Manners, I. *Chem. Mater.* **1990**, *2*, 425.

(15) Elschenbroich, C.; Salzer, A. *Organometallics: A Concise Introduction*; VCH: Weinheim, 1992.

(16) The Cr–(η -C₆H₆) bond energy of Cr(η -C₆H₆)₂ is ~170 kJ/mol (see ref 15, p 345), and we have found that attempted TROP of Cr(η -C₆H₆)₂-SiMe₂ at 170 °C yields Cr metal and Ph₂SiMe₂ as exclusive products. Hultsch, K.; Nelson, J. M.; Lough, A. J.; Manners, I., to be submitted. For the synthesis and structural characterization of an analogous species, see: Elschenbroich, C.; Hurley, J.; Metz, B.; Massa, W.; Baum, G. *Organometallics* **1990**, *9*, 889–897.

(17) For the preparation of **3**, see: Pudelski, J. K.; Foucher, D. A.; Honeyman, C. H.; Lough, A. J.; Manners, I.; Barlow, S.; O'Hare, D. *Organometallics* **1995**, *14*, 2470.

(18) Poly(ferrocenylsilane) **4** was fully characterized and gave satisfactory elemental analysis; see supporting information.

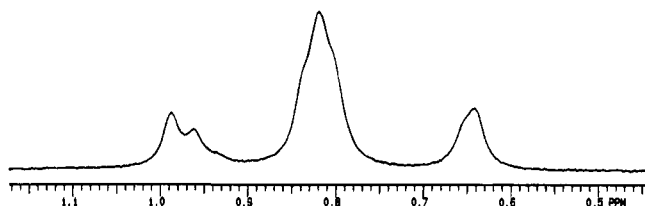


Figure 1. Si-Me region expansion of the ^1H NMR spectrum (200 MHz, C_6D_6) of **4**.

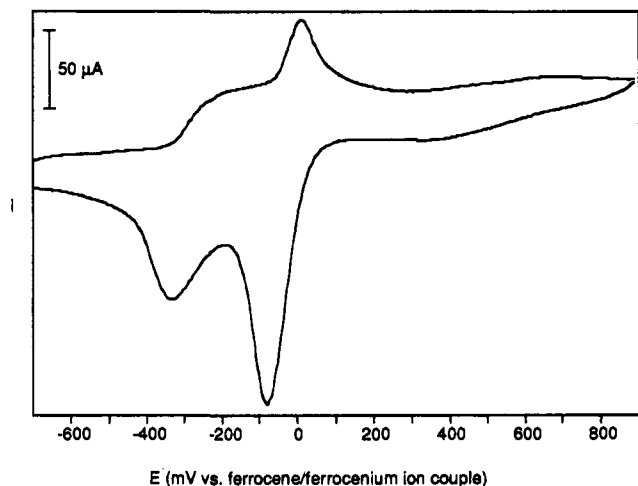


Figure 2. Cyclic voltammogram of a 5×10^{-3} M CH_2Cl_2 solution of **4** which was also 0.1 M in $[\text{Bu}_4\text{N}][\text{PF}_6]$, obtained at room temperature at a scan rate of 250 mV/s.

1:2:1 integral ratio centered at 0.98, 0.82, and 0.64 ppm, respectively (Figure 1). Similarly, ^{29}Si NMR analysis of **4** gave three sets of resonances, in an $\sim 1:2:1$ intensity ratio, centered at -4.05 , -6.42 , and -6.77 ppm, and ^{13}C NMR also showed three sets of resonances in the SiMe_2 region. These results clearly indicated the presence of three types of silicon environments in **4** in a statistical ratio and therefore showed that TROP of **3** proceeds via nonselective cleavage of $\text{Si}-\text{Cp}^{\text{H}}$ and $\text{Si}-\text{Cp}^{\text{Me}}$ bonds.

Analysis of **4** by cyclic voltammetry clearly confirmed that all of the iron atoms exist in a $\text{Cp}^{\text{H}}\text{FeCp}^{\text{Me}}$ environment. Cyclic voltammograms of a CH_2Cl_2 solution of **4** showed two oxidation waves of equal intensity ($E_{1/2} = -0.24$ and -0.03 V) with shapes that were modified by electrode adsorption effects (Figure 2). This two-wave response is completely analogous to that previously reported for other poly(ferrocenylsilanes) and is consistent with initial oxidation at alternating iron sites along the polymer backbone, followed by subsequent oxidation, at a higher potential, of the iron centers in between.^{3,6,11} Thus, the cyclic voltammograms confirm the presence of only a single

type of iron environment in **4**. Moreover, the observed $E_{1/2}$ value of -0.24 V found for the first oxidation wave is consistent with the presence of iron atoms in a $\text{Cp}^{\text{H}}\text{FeCp}^{\text{Me}}$ environment.¹⁹

Given the high molecular weights of the poly(ferrocenylsilanes) prepared via TROP, identification of the melt initiators is likely to be difficult since they are present in minute concentrations. However, additional experiments suggest that the bond cleavage during TROP of silicon-bridged [1]ferrocenophanes is not homolytic in nature. We obtained high molecular weight **2** via TROP of **1** in the presence of catalytic and stoichiometric quantities of radical trap butylated hydroxytoluene (BHT) with no observed rate inhibition. Indeed, TROP of **1** even proceeds smoothly in molten BHT (mp = $69-70$ $^\circ\text{C}$). In all of these experiments, conversion was complete, and the only species observed other than **2** was unreacted BHT.

Our BHT studies strongly suggest that TROP occurs via heterolytic cleavage of the $\text{Si}-\text{Cp}$ bond rather than a homolytic process. Such cleavage might be initiated by minute traces of nucleophilic impurities such as water.²⁰ Alternatively, thermal heterolytic cleavage might afford a small population of zwitterionic species with positive charge at silicon and negative charge at the cyclopentadienyl ring, which could then initiate chain propagation by attack on uncleaved $\text{Si}-\text{cyclopentadienyl}$ bonds. Indeed, such a mechanism has been proposed for the TROP of silacyclobutanes and related species.²¹

We are now extending our mechanistic investigations to other [1]- and [2]metallocenophanes.

Acknowledgment. We thank the donors of the Petroleum Research Fund, administered by the American Chemical Society, for financial support of this work, and I.M. thanks the Alfred P. Sloan Foundation for a fellowship (1994-96).

Supporting Information Available: Full preparative details, complete characterization data, and analytical data for **4**; complete experimental details and product characterization data for BHT studies (4 pages). This material is contained in many libraries on microfiche, immediately follows this article in the microfilm version of the journal, can be ordered from the ACS, and can be downloaded from the Internet; see any current masthead page for ordering information and Internet access instructions.

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(19) The half-wave oxidation potentials of methylated ferrocene derivatives are lowered by ~ 55 mV per methyl substituent, relative to ferrocene. See: Gassman, P. G.; Macomber, D. W.; Hershberger, J. W. *Organometallics* **1983**, *2*, 1470.

(20) We have observed facile ROP reactions of **1** in solution at room temperature in the presence of anionic initiators such as BuLi. See: Rulkens, R.; Ni, Y.; Manners, I. *J. Am. Chem. Soc.* **1994**, *116*, 12121. Ring-opening reactions of **1** also occur in the presence of nucleophilic species such as methanol. See: Fischer, A. B.; Kinney, J. B.; Staley, R. H.; Wrighton, M. S. *J. Am. Chem. Soc.* **1979**, *101*, 6501.

(21) 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.