Organometallics **2005,** *24,* 1053−1055

Synthesis, X-ray Structure, and Ring-Opening Polymerization of Pentacoordinate Silicon-Bridged [1]Ferrocenophane

Yasuo Hatanaka,*,† Shingo Okada,‡ Tatsuya Minami,† Midori Goto,‡ and Kayori Shimada‡

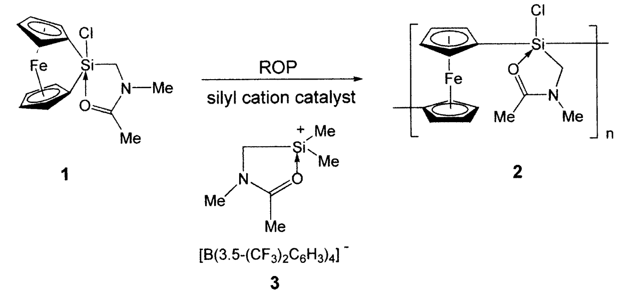
Department of Applied Chemistry, Graduate School of Engineering, Osaka City University, Sugimoto 3-3-138, Sumiyoshi-ku, Osaka 558-8585, Japan, and National Institute of Advanced Industrial Science and Technology, Tsukuba Central 5, Higashi 1-1-1, Tsukuba, Ibaraki 305-8565, Japan

Received November 29, 2004

Summary: The cationic ring-opening polymerization of cyclic pentacoodinate sila[1]ferrocenophanes was carried out in dichloromethane to give poly(ferrocenylsilanes) having pentacoordinate silicon moieties in the polymer backbone. The silyl cation gave the best results as an initiator for the polymerization, affording pentacoordinate poly(ferrocenylsilane) (M_w is 9.0×10^3) in high yields.

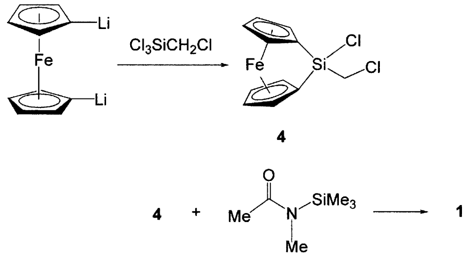
Poly(ferrocenylsilanes), which have a backbone consisting of alternating ferrocene and organosilane units, are attracting considerable interest as materials with new and potentially useful properties.[1] The electronic structure of silicon-containing polymers can be affected by the coordination number and valence state of the silicon atoms.[2] For example, we have recently reported that the incorporation of pentacoordinate silicon moieties into the backbone of oligosilanes dramatically reduces the excitation energies of the Si−Si bonds.[3] Although incorporation of hypervalent silicon moieties into polymer structures is expected to alter the electronic properties of the polymers, the synthesis of poly(ferrocenylsilanes) containing hypercoordinate silicon in the polymer backbone has not been realized yet.[4] We report herein the synthesis and characterization of the pentacoordinate sila[1]ferrocenophane **1** as a monomer and its ring-opening polymerization (ROP) promoted by silyl cation catalyst **3** (Scheme 1).

Scheme 1



The reaction of dilithioferrocene with (chloromethyl)trichlorosilane in the presence of TMEDA (tetramethylethylenediamine) in ether afforded the tetracoordinate silicon-bridged [1]ferrocenophane **4** in 43% yield after recrystallization from hexane (−20 °C) (Scheme 2). The structure of **4** was confirmed by a single-crystal X-ray diffraction study (Figure 1).[5] Treatment of **4** with *N*-methyl-*N*-(trimethylsilyl)acetamide in hexane at room temperature gave the pentacoordinate silicon-bridged [1]ferrocenophane **1** in 89% yield.[3a] Dark red crystals of **1** suitable for X-ray diffraction were prepared by recrystallization from dichloromethane (−40 °C).[6]

Scheme 2



---

* To whom correspondence should be addressed. E-mail: hatanaka@a-chem.eng.osaka-cu.ac.jp.

† Osaka City University.

‡ National Institute of Advanced Industrial Science and Technology.

(1) For reviews, see: (a) Manners, I. *Can. J. Chem.* **1998**, *76*, 371. (b) Kulbaba, K.; Manners, I. *Macromol. Rapid Commun.* **2001**, *22*, 711.

(2) (a) Tandura, S. N.; Voronkov, M. G.; Alkseev, N. V. *Top. Curr. Chem.* **1986**, *131*, 99. (b) Chuit, C.; Corriu, R. J. P.; Reye, C.; Young, J. C. *Chem. Rev.* **1993**, *93*, 1371. (c) Holmes, R. R. *Chem. Rev.* **1996**, *96*, 927.

(3) (a) El-Sayed, I.; Hatanaka, Y.; Muguruma, C.; Shimada, S.; Tanaka, M.; Koga, N.; Mikami, M. *J. Am. Chem. Soc.* **1999**, *121*, 5095−5096. (b) Muguruma, C.; Koga, N.; Hatanaka, Y.; El-Sayed, I.; Mikami, M.; Tanaka, M. *J. Phys. Chem. A* **2000**, *104*, 4928. (c) Hatanaka, Y. *J. Organomet. Chem.* **2003**, *685*, 207.

(4) Manners and co-workers have reported the synthesis of pentacoordinate silicon-bridged [1]ferrocenophane having pseudo-trigonal-bipyramidal geometry at the silicon atom: (a) Jäkle, F.; Vejzovic, E.; Nicole Power-Billard, K.; MacLachlan, M. J.; Lough, A. J.; Manners, I. *Organometallics* **2000**, *19*, 2826. Thermal ring-opening polymerization of this compound under reflux conditions in xylene gave poly(ferrocenylsilane) with tetracoordinate silicon atoms in the polymer backbone: (b) Jäkle, F.; Wang, Z.; Manners, I. *Macromol. Rapid Commun.* **2000,** *21*, 1291.

(5) Crystal data for **4**: $C_{11}H_{10}Cl_2SiFe$, $M_r = 297.04$, orthorhombic, $a = 9.625(5)$ Å, $b = 15.549(2)$ Å, $c = 7.753(3)$ Å, $U = 1160.2(6)$ Å^3, space group $P2_12_12_1$ (No. 19), $Z = 4$, $D_c = 1.700$ g cm^{-3}, μ(Mo Kα) = 1.821 mm^{-1}, 1454 observed reflections ($I > 3\sigma(I)$), R1 = 0.023, wR2 = 0.0326, Rigaku AFC7R diffractometer, Mo Kα radiation ($\lambda = 0.710\ 69$ Å), graphite monochromator. The file CCDC 255494 contains the supplementary crystallographic data for compound **4**. These data can be obtained free of charge via http://www.ccdc.cam.ac.uk/cgi-bin/catreq.cgi (or from the Cambridge Crystallographic Centre, 12 Union Road, Cambridge CB21EZ, U.K.; fax (+44)1223-336-033; e-mail deposit@ccdc.cam.ac.uk).

10.1021/om040132r CCC: $30.25

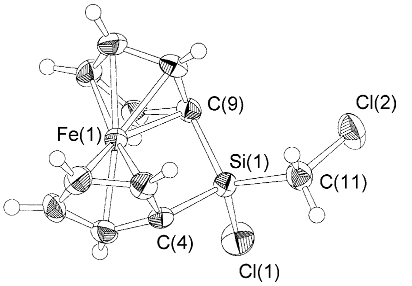


Figure 1. X-ray structure of **4**. Selected interatomic distances (Å), bond lengths (Å), and angles (deg): Fe(1)- - -Si(1) = 2.631(1); Si(1)−C(9) = 1.864(3), Si(1)−C(4) = 1.865(3), Si(1)−C(11) = 1.860(3), Si(1)−Cl(1) = 2.052(1); C(4)−Si(1)−C(9) = 99.1(1), C(1−5)//C(6−10) = 19.08.

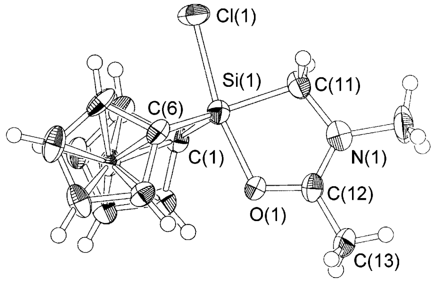


Figure 2. X-ray structure of **1**. Selected interatomic distances (Å), bond lengths (Å), and angles (deg): Fe(1)- - -Si(1) = 2.708(3); Si(1)−C(1) = 1.878(9), Si(1)−C(6) = 1.891(9), Si(1)−C(11) = 1.905(9), Si(1)−Cl(1) = 2.264(4), Si(1)−O(1) = 1.920(6); C(1)−Si(1)−C(6) = 95.6(4), C(1)−Si(1)−C(11) = 126.7(4), C(6)−Si(1)−C(11) = 137.2(4), Cl(1)−Si(1)−O(1) = 167.9(2), Cl(1)−Si(1)−C(1) = 97.2(3), Cl(1)−Si(1)−C(6) = 96.2(3), Cl(1)−Si(1)−C(11) = 85.7(3); C(1−5)//C(6−10) = 20.29.

The X-ray analysis of compound **1** revealed an almost ideal trigonal-bipyramidal (TBP) structure (Figure 2).[7,8] The TBP character of the silicon atom of **1** is markedly high; the %TBP$_e$ value for **1** estimated from the three equatorial-to-equatorial angles (C(1)−Si−C(6), C(6)−Si−C(11), and C(1)−Si−C(11)) is 98%.[9] The Si−Cl bond length (2.264(4) Å) and the Si−O distance (1.920(6) Å) are typical for [3 + 2] TBP coordination.[7]

The C(Cp)−Si−C(Cp) bond angle of 95.6(4)° in the pentacoordinate sila[1]ferrocenophane **1** is significantly smaller than that in the tetracoordinate sila[1]ferrocenophane **4** (99.1(1)°), and concomitantly, the Fe- - -Si distance in **1** is longer than that in **4** (**1**, 2.708(3) Å; **4**, 2.631(1) Å). The *ipso*-C−Si bonds of **1** (C(1)−Si = 1.878(9) Å, C(6)−Si = 1.891(9) Å) are considerably longer than those of **4** (C(4)−Si = 1.856(3) Å, C(9)−Si = 1.864(3) Å), suggesting that the *ipso*-C−Si bonds of the pentacoordinate sila[1]ferrocenophane **1** are weaker than those of the tetracoordinate sila[1]ferrocenophane **4**. In fact, the *ipso*-C−Si bonds of **1** are easily cleaved to initiate ring-opening polymerization in the presence of the silyl cation catalyst **3**, whereas **4** is virtually inert under the same reaction conditions.

The interesting feature of the ^{13}C NMR spectrum of **1** is that the *ipso-C*(Cp) resonance in **1** is shifted strongly downfield in comparison with that in **4** (**1**, δ 47.5; **4**, δ 31.4 in CD_2Cl_2),[10] which is indeed at lower field than for any silicon-bridged [1]ferrocenophane investigated to date.[4a]

The ^{29}Si NMR spectra of **1** showed that the chemical shift of the pentacoordinate silicon atom (−69.7 ppm in CD_2Cl_2) is shifted markedly upfield by ca. 70 ppm from that of the tetracoordinate sila[1]ferrocenophane **4** (−0.29 ppm), supporting the high pentacoordinate character of the silicon atom in **1**.[11]

When monomer **1** was allowed to react with a catalytic amount of silylium salt **3**[12] (1.0 mol %) in dichloromethane, cationic ring-opening polymerization took place at room temperature to furnish the corresponding polymer **2** (Scheme 1). To the best of our knowledge, cationic ring-opening polymerization of sila[1]ferrocenophanes is extremely rare,[13] while these compounds have been reported to smoothly undergo thermal or anionic ring-opening polymerization.[1] ^{1}H NMR monitoring of the reaction showed that the completion of the polymerization needed a period of 14 days. The use of other Lewis acid catalysts such as trimethylsilyl triflate, iodotrimethylsilane, and $BF_3{\cdot}OEt_2$ under the same reaction conditions was less effective, leading to sluggish reaction. Dissolution of crude polymer in dichloromethane followed by precipitation with dry hexane afforded the analytically pure poly(ferrocenylsilane) **2** as an orange solid in 53% yield.[14] This material is highly soluble in dichloromethane and THF.

Evidence for the successful polymerization was provided by measurement of the weight-average molar mass M_w using a low-angle laser light scattering method

---

(6) Crystal data for **1**: $C_{14}H_{16}ClNOSiFe$, M_r = 333.67, orthorhombic, a = 12.493(3) Å, b = 14.339 (4) Å, c = 7.544(3) Å, U = 1351.5(7) Å^3, space group $Pna2_1$ (No. 33), Z = 4, D_c = 1.640 g cm^{-3}, μ(Mo Kα) = 1.390 mm^{-1}, 964 observed reflections ($I > 2\sigma(I)$), R1 = 0.040, wR2 = 0.1509, Rigaku AFC7R diffractometer, Mo Kα radiation (λ = 0.710 69 Å), graphite monochromator. The file CCDC 255493 contains the supplementary crystallographic data for compound **1**. These data can be obtained free of charge via http://www.ccdc.cam.ac.uk/cgi-bin/catreq.cgi (or from the Cambridge Crystallographic Centre, 12 Union Road, Cambridge CB21EZ, U.K.; fax (+44)1223-336-033; e-mail deposit@ccdc.cam.ac.uk).

(7) For related X-ray structures of pentacoordinate silicon compounds see: (a) Hillyard, R. W., Jr.; Ryan, C. M.; Yoder, C. H. *J. Organomet. Chem.* **1978**, *153*, 369. (b) Yoder, C. H.; Ryan, C. M.; Martin, G. F.; Ho, P. S. *J. Organomet. Chem.* **1980**, 1*90*, 1 and references therein. (c) El-Sayed, I.; Hatanaka, Y.; Onozawa, S.; Tanaka, M. *J. Am. Chem. Soc.* **2001**, *123*, 3597. (d) Pestunovich, V. A.; Valery, F. S.; Voronkov, M. G. In *Progress in Organosilicon Chemistry*; Marciniec, B., Chojnowski, J., Eds.; Gordon and Breach: Basel, Switzerland, 1995; pp 69−82.

(8) For X-ray structures of sila[1]ferrocenophanes see: (a) Stoeckli-Evans, H.; Osborne, A. G.; Whiteley, R. H. *Helv. Chim. Acta* **1976**, *59*, 2402. (b) Butler, I. R.; Cullen, W. R.; Retting, S. J. *Can. J. Chem.* **1987**, *65*, 1452. (c) Finckh, W.; Tang. B.-Z.; Foucher, D. A.; Zamble, D. B.; Ziembinski, R.; Lough, A.; Manners, I. *Organometallics* **1993**, *12*, 823. See also ref 4a.

(9) For the %TBP$_e$ value, see: Tamao, K.; Hayashi, T.; Ito, Y.; Shiro, M. *Organometallics* **1992**, *11*, 2099.

(10) Selected spectroscopic data are as follows. For **1**: ^{1}H NMR (300 MHz, CD_2Cl_2) δ 4.49, 4.46, 4.42, 4.23 (4 × m, 4 × 2 H, Cp H), 3.19 (s, 3 H, NCH_3), 3.17 (s, 2H, CH_2), 2.29 (s, 3 H, $COCH_3$); $^{13}C\{^1H\}$ NMR (75.5 MHz, CD_2Cl_2) δ 174.8 (CO), 81.8 (Cp), 79.2 (Cp), 78.5 (Cp), 77.0 (Cp), 47.5 (*ipso*-Cp), 44.0 (CH_2), 37.1 (NCH_3), 17.3 (CH_3); ^{29}Si NMR (59.6 MHz, CD_2Cl_2) δ −69.7; For **4**: ^{1}H NMR (300 MHz, C_6D_6) δ 4.29 (s, 4 H, Cp H), 4.12 (s, 2 H, Cp H), 3.95 (s, 2 H, Cp H), 2.84 (s, 2 H, CH_2); $^{13}C\{^1H\}$ NMR (75.5 MHz, C_6D_6) δ 79.1 (Cp), 79.0 (Cp), 76.0 (Cp), 74.6 (Cp), 31.4 (*ipso*-Cp), 28.2 (CH_2); ^{29}Si NMR (59.6 MHz, C_6D_6) δ −0.27.

(11) The ^{29}Si chemical shifts for pentacoordinate silicon usually exhibit an upfield shift relative to tetracoordinate silicon: Kost, D.; Kalikhman, I. In *The Chemistry of Organic Silicon Compounds*; Rappoport, Z., Apeloig, Y., Eds.; Wiley: Chichester, England, 1998; Vol. 2, pp 1339−1445.

(12) Hatanaka, Y.; Reddy, A. C. S.; Tanaka, M.; Onozawa, S. Jpn. Kokai Tokkyo Koho JP2002265477 2002; *Chem. Abstr.* **2003**, *137*, 248114.

(13) Baumgartner, T.; Jäkle, F.; Rulkens, R.; Zech, G..; Lough, A. J.; Manners, I. *J. Am. Chem. Soc.* **2002**, *124*, 10062−10070.

(14) Selected spectroscopic data for **2** are as follows: ^{1}H NMR (300 MHz, CD_2Cl_2) δ 3.7−4.9 (m, 8 H), 2.5−3.7 (m, 5 H), 1.5−2.5 (m, 3 H); ^{29}Si NMR (59.6 MHz, CD_2Cl_2) δ −57.31, −59.78.

in dichloromethane. Refractive index increment measurements were performed at five different polymer concentrations in CH_2Cl_2 at 20 °C, and a value of d*n*/d*c* = 0.152 was obtained. The M_w and the second virial coefficient A_2 were determined from the Rayleigh−Debye equation, where values of $M_w = 9.0 \times 10^3$ and $A_2 = 1.16 \times 10^{-3}$ mol cm^2 g^{-2} were obtained. The ^{29}Si NMR spectra of polymer **2** displayed two peaks at −57.31 and −59.78 ppm in CD_2Cl_2, indicating the high pentacoordinate character of the silicon atoms involved in **2**.

The pentacoodinate sila[1]ferrocenophane **1** exhibits metal d−d HOMO−LUMO type transitions at 430 nm (ϵ = 233 cm^{-1} M^{-1}) and at 320 nm (ϵ = 389 cm^{-1} M^{-1}), which have been assigned to overlapping $^1A_{1g} \rightarrow {}^1E_{2g}$ and $^1A_{1g} \rightarrow a^1E_{1g}$ transitions and a $^1A_{1g} \rightarrow b^1E_{1g}$ transition, respectively.[15] By analogy with the UV spectral assignments for **1**, the absorption of the pentacoordinate polymer **2** in the 300−600 nm region can be considered to arise from electronic transitions with HOMO−LUMO character. The pentacoordinate polymer **2** exhibits overlapping $^1A_{1g} \rightarrow {}^1E_{2g}$ and $^1A_{1g} \rightarrow a^1E_{1g}$ transitions at 400−500 nm, which are only slightly different from those of the monomer **1**. In contrast, the $^1A_{1g} \rightarrow b^1E_{1g}$ transition of the polymer **2** at 330 nm experiences a slight bathochromic shift and markedly increases in intensity in comparison to that of the monomer **1** (**2**, λ = 330 nm, ϵ = 1305 cm^{-1} M^{-1}; **1**, λ = 320 nm, ϵ = 389 cm^{-1} M^{-1}). This spectral change seems to reflect the change of the electronic structure provided by the cationic ring-opening polymerization. Thus, polymerization of **1** has been found to strengthen the oscillator strength of the $^1A_{1g} \rightarrow b^1E_{1g}$ d−d transition in the ferrocene moiety.

A detailed comparison of the UV spectrum of the pentacoordinate polymer **2** with that of tetracoordinate silicon-containing poly(ferrocenylsilanes) such as [Fe(η-C_5H_4)$_2$Si(*n*-Hex)$_2$]$_n$ (**5**)[16] reveals an appreciable difference in spectral properties between pentacoordinate and tetracoordinate polymers. Polymer **5** exhibits a $^1A_{1g} \rightarrow b^1E_{1g}$, d−d transition at 330−340 nm as an extremely weak absorption, which could not be accurately resolved as a weak shoulder peak.[16] In contrast, the same electronic transition of the pentacoordinate polymer **2** appears at λ = 330 nm as a relatively intense absorption (ϵ = 1305 cm^{-1} M^{-1}). It is probable that the appearance of the intense absorption in the near-UV region is due to the electronic perturbation provided by the incorporation of pentacoordinate silicon moieties into the polymer backbones. However, the precise mechanism of this electronic perturbation is not clear at the present stage. Currently, we are studying the electronic properties of various types of hypercoordinate poly(ferrocenylsilanes) as well as the synthesis of hypercoordinate sila[1]-ferrocenophanes.

Acknowledgment. This work was partially supported by a Grant-in-Aid for Scientific Research from the Japan Society for the Promotion of Science.

Supporting Information Available: Text giving synthetic procedures for **1**−**4** and tables giving details on the X-ray crystal structure analysis of **1** and **4**. This material is available free of charge via the Internet at http://pubs.acs.org.

OM040132R

---

[15] Sohn, Y. S.; Hendrickson, D. N.; Gray, H. B. *J. Am. Chem. Soc.* **1971**, *93*, 3603.

[16] Foucher, D. A.; Ziembinski, R.; Tang, B.-Z.; Macdonald, P. M.; Masson, J.; Jaeger, R.; Vancso, J.; Manners, I. *Macromolecules* **1993**, *26*, 2878.