

Formation of 1,1,12,12-Tetramethyl[1.1]silaferrocenophane and poly(ferrocenylsilane) in the reaction of ferrous chloride with the dilithium salt of dicyclopentadienyldimethylsilanes

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Received 6 April 1994; in revised form 1 June 1994

Abstract

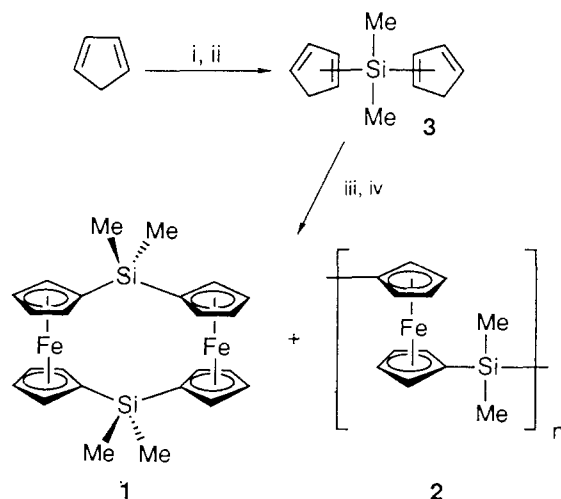
1,1,12,12-Tetramethyl[1.1]silaferrocenophane (**1**) and poly(ferrocenylsilane) (**2**) were formed as the major products in the reaction of FeCl_2 with the dilithium salt of $(\text{C}_5\text{H}_5)_2\text{SiMe}_2$, and the X-ray crystallography for **1** revealed its molecular structure of an anti conformation.

Keywords: Ferrocene; Silicon; X-ray diffraction; Polysilane; Cyclopentadienyl; Polymer

Continuous effort has been devoted to the development of new synthetic routes to macromolecules which contain inorganic elements or organometallic units [1–3]. For examples, ferrocenophanes and polymers containing ferrocene units are interesting research subjects with respect to their potentially useful properties [4]. As a kind of silicon-bridged organometallic polymer poly(ferrocenylsilane) has been prepared by using monomeric ferrocene derivatives as starting materials, such as [1]silaferrocenophanes in a thermal ring-opening polymerization or an anionic ring-opening oligomerization [5–9], and 1,1'-dilithioferrocene in a polycondensation reaction with dialkyldichlorosilanes [10].

In this paper, we report the formation of 1,1,12,12-tetramethyl[1.1]silaferrocenophane (**1**), which is the first example of a silicon-bridged [1.1]ferrocenophane, as well as the poly(ferrocenylsilane) **2** in the reaction of ferrous chloride with the dilithium salt of dicyclopentadienyldimethylsilane (Scheme 1). The molecular structure of **1** was characterized by various spectroscopic methods as well as X-ray crystallography. The spectral and physical properties of the polymer **2** were examined in comparison with the known high molecular weight poly(ferrocenylsilane) [5,7].

An isomeric mixture of dicyclopentadienyldimethylsilanes (**3**) was accessible from the reaction of dichlorodimethylsilane with 2 equiv. of cyclopentadienyllithium [11,12]. The dilithium salt of **3** was reacted with ferrous chloride (1.5 equiv.) in THF at 70°C for 12 h to give a mixture (combined yield: 73%) which contained **1** and **2** as the major products in about 1:2



Scheme 1. Reagents and conditions: (i) $n\text{BuLi}$, THF, -78°C , 2 h; (ii) Me_2SiCl_2 , THF, -78 to 25°C , 4 h; (iii) $n\text{BuLi}$ (2 equiv.), THF, -78°C , 2 h; (iv) FeCl_2 , THF, reflux, 18 h.

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ratio. The combined yield of the products **1** and **2** was reduced by using more or less than 1.5 equiv of FeCl_2 . Precipitation from a concentrated THF solution of the mixture into hexane gave relatively high molecular weight poly(ferrocenylsilanes) as a yellow powder in 7.3% yield. Then the ferrocenophane **1** was isolated from the hexane-soluble portion as orange crystals (mp 210–213°C) in 21.3% yield by column chromatography (hexane/ethyl acetate 15:1) on silica gel.

The spectral properties of **2** are almost identical to those reported previously [5,13]. Gel permeation chromatography indicated that the solid poly(ferrocenylsilane) possessed the weight-average molecular weight (M_w) of 4900 and the number-average molecular weight (M_n) of 4100 relative to polystyrene standards for column calibration. Those of the polymer, which was obtained from the hexane soluble filtrate, are 2900 (M_w) and 2200 (M_n), respectively.

The ^1H NMR spectrum of **1** (in C_6D_6) showed two sets of multiplets for the cyclopentadienyl protons at 4.31 and 4.25 ppm and a sharp singlet at 0.39 ppm for the methyl groups attached to the silicon in the expected 4:4:6 ratio. The ^{13}C NMR spectrum of **1** (in C_6D_6) showed four resonances at 73.9, 71.5, 70.9, and 2.1 ppm, of which the resonance at 71.5 ppm can be assigned to the cyclopentadienyl carbon attached to silicon. The ^{29}Si NMR spectrum of **1** (in C_6D_6) showed a singlet at -6.47 ppm. The UV/visible spectrum of **1** (in THF) contained the band in the visible region at 464 nm ($\epsilon = 390 \text{ M}^{-1} \text{ cm}^{-1}$) which showed the characteristic bathochromic shift and increased intensity relative to the long wave-length band of ferrocene at 444 nm ($\epsilon = 100 \text{ M}^{-1} \text{ cm}^{-1}$). The results from the elemental analysis and the mass spectroscopy for **1** were consistent with the structure of 1,1,12,12-tetramethyl[1.1]silaferrrocenophane.

The molecular structure of **1** was established by X-ray crystallography (Fig. 1) [14]. The molecule itself possesses a center of inversion and an anti conformation. The inversion symmetry indicates that the two central axes through each of the ferrocenylene units are parallel. The interplanar angle between the two Cp rings of each ferrocenylene moiety is 4.7° , and the two rings are nearly eclipsed with an average staggering angle of 13.6° . The iron–carbon distances are in the range of 2.032–2.074(3) Å while the average distance (2.047 Å) is close to the value of 2.045 Å found for ferrocene [15]. For the bridging Si–C bonds, the average bond length and the bond angle are 1.860(3) Å and $112.9(1)^\circ$, respectively, which are the values between those of 1,12-dimethyl[1.1]ferrocenophane (1.647 Å and 121.3°) [16], and those of 1,1,12,12-tetra-*n*-butyl[1.1]-stannaferrocenophane (2.136 Å and 110.0°) [17,18]. The Fe, Fe distance (5.163 Å) in **1** is also in between the values of the carbon analogue (4.816 Å) and the tin analogue (5.50 Å).

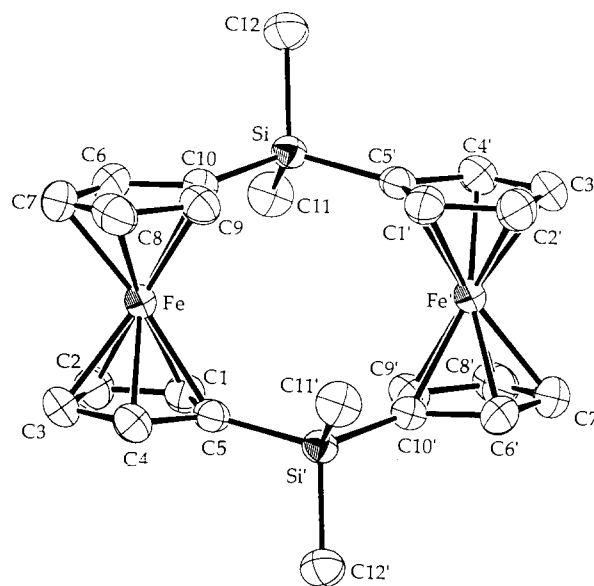


Fig. 1. Molecular structure of **1**. Fe–Fe', 5.163; Fe–C(5), 2.074(3); Fe–C(4), 2.040(3); Fe–C(3), 2.045(4); Fe–C(7), 2.035(3); Fe–C(6), 2.032(3); Fe–C(10), 2.068(3); Si–C(10), 1.861(3); Si–C(11), 1.858(3); Si–C(12), 1.863(3); C(5)–C(4), 1.445(4); C(4)–C(3), 1.413(5); C(3)–C(2), 1.413(5) Å. C(5)–Fe–C(10), $120.1(1)^\circ$; C(3)–Fe–C(7), $104.3(1)^\circ$; C(5)–Si–C(10'), $112.9(1)^\circ$; C(5)–Si–C(11'), $111.4(1)^\circ$; C(5)–Si–C(12'), $106.6(1)^\circ$; Fe–C(5)–Si', $134.7(2)^\circ$; C(11)–Si–C(12), $108.3(2)^\circ$; C(1)–C(5)–Si', $129.6(2)^\circ$; C(4)–C(5)–Si', $125.0(2)^\circ$.

Cyclic voltammetry was performed with a stationary Pt electrode for a preliminary investigation of the electrochemistry of **1**. The measurements were carried out on 1 mM solutions containing 0.1 M tetrabutylammonium tetrafluoroborate as supporting electrolytes in CH_2Cl_2 . Two reversible oxidation processes were observed at -0.02 and 0.21 V (vs ferrocene). The peak-to-peak separation ($\Delta E_{1/2}$) implicates the considerable interaction between the two Fe sites and the value of 0.23 V is higher than those of the carbon analogue and the tin analogue [17].

Acknowledgments

We thank Dr. Hongdoo Kim for his help in obtaining cyclic voltammograms and the Research Institute of Industrial Science and Technology for the financial support.

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- [13] For polymer 2: UV/vis (THF) λ_1 444 nm ($\epsilon_1 = 198 \text{ M}^{-1} \text{ cm}^{-1}$), λ_2 246 nm ($\epsilon_2 = 5500 \text{ M}^{-1} \text{ cm}^{-1}$); $^1\text{H NMR}$ (C_6D_6) δ 4.26 (s, 4 H, Cp), 4.10 (s, 4 H, Cp), 0.52 ppm (s, 6 H, CH_3); $^{13}\text{C NMR}$ (C_6D_6) δ 73.6 (Cp), 71.9 (Cp, C-Si), 71.7 (Cp), -0.52 ppm (SiMe_3)
- [14] Crystal data for 1: $\text{C}_{24}\text{H}_{28}\text{Fe}_2\text{Si}_2$, $M_r = 484.36$, orange, $0.5 \times 0.4 \times 0.2 \text{ mm}^3$, monoclinic, $P2_1/n$, $a = 8.7571(14)$, $b = 12.1469(10)$, $c = 10.329(3) \text{ \AA}$, $\beta = 90.631(9)^\circ$, $V = 1098.7(4) \text{ \AA}^3$, $Z = 2$, $D_c = 1.464 \text{ g cm}^{-3}$, $\mu = 14.35 \text{ cm}^{-1}$, $T = 295 \text{ K}$; 2038 unique reflections measured; 1560 reflections observed ($I > 3\sigma(I)$); $R(F) = 0.028$, $R_w(F) = 0.029$, G.O.F. = 0.40. The crystals were sealed in capillaries before the intensity data were collected with an Enraf-Nonius CAD4 diffractometer using monochromated $\text{Mo K}\alpha$ radiation ($\lambda(\text{K}\alpha) = 0.71073 \text{ \AA}$). The structures were solved by Patterson and difference Fourier methods and refined by full-matrix least-squares method. Non-hydrogen atoms were refined anisotropically. Hydrogen atoms were refined isotropically with isotropic thermal parameters of 1.2 times that of attached atoms.
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