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Organometallic Nonlinear Optical Polymers. 3. Copolymerization of Bridged Bis(ferrocenyl) and Bis(cyanoacetate) Monomers via the Knoevenagel Condensation

Michael E. Wright* and Matthew S. Sigman

Department of Chemistry & Biochemistry, Utah State University, Logan, Utah 84322-0300

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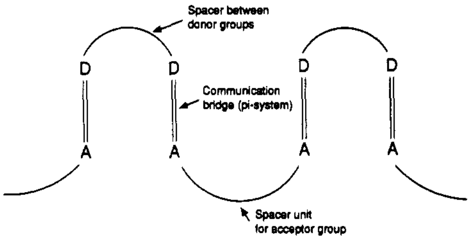
ABSTRACT: The bridged bis(ferrocenyl) monomer $[\{\eta^5\text{-}C_5H_4CHO\}Fe\{\eta^5\text{-}C_5H_4\}]_2SiMe_2$ (1) was prepared in two steps from $\{\eta^5\text{-}C_5H_4SnBu_3\}_2Fe$. A single-crystal molecular structure was obtained for monomer 1. The bis(cyanoacetate) monomers $CNCH_2CO_2(CH_2)_nO_2CCH_2CN$ (2) [where n = 4, 6, and 8] were prepared in high yield by reacting ethyl cyanoacetate with the appropriate diol in the presence of $Ti(OC_4H_9)_4$. Knoevenagel polycondensation [K_2CO_3, THF, 50 °C] of 1 and 2 afforded a new class of organometallic accordion copolymers. Average molecular weights for the accordion copolymers ranged from 9100 to 26 600 with polydispersities of ~2.1. The polymers were soluble in organic solvents and thus fully characterized by spectroscopic methods. The polymers were also characterized by thermal analysis and analytical data. The Knoevenagel polycondensation reaction appeared to produce a mixture of *E* and *Z* isomers (9/1, respectively); however, isomerically enriched polymer (i.e., 98% *E* isomer) was obtained through selective precipitation.

Introduction

In the previous paper[1] we presented the synthesis of linear organometallic main-chain nonlinear optical (NLO) polymers. Our research has continued to focus on ferrocene-based NLO polymers because of the large experimental β values (up to 200 times that of urea) obtained by Marder and co-workers using crystalline ferrocene complexes.[2] The ability to selectively functionalize the cyclopentadienyl rings of ferrocene has given us the ability to prepare elaborate organometallic NLO-phores.[3] Lindsay and co-workers recently presented the synthesis of a new class of main-chain organic NLO polymers.[4] For this new class of NLO materials the polymer backbone will be aligned into an accordion shape.[5] To date, this approach has not been used in the area of organometallic polymeric NLO materials.[6]

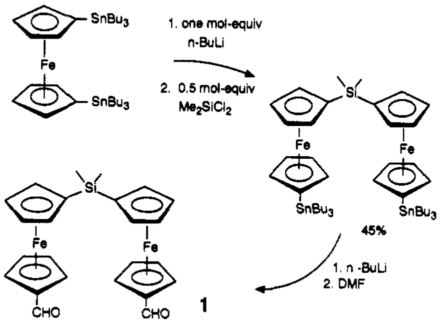


Main Chain Accordion NLO Polymer

In this paper we present the synthesis and characterization of organometallic polymers with the potential of adopting the accordion macrostructure. As we saw in the previous paper, the use of the Knoevenagel condensation appears to be the most effective manner to prepare polymers of good molecular weight and tractability.

Results and Discussion

Monomer Synthesis and Characterization. Selective monotransmetalation of the ferrocene complex $\{\eta^5\text{-}C_5H_4SnBu_3\}_2Fe$[7] followed by reaction with $^1/_2$ mol equiv of dimethyldichlorosilane affords the bridged ferrocene system in 45% isolated yield (eq 1). Separation of $\{(\eta^5\text{-}C_5H_4SnBu_3)Fe(\eta^5\text{-}C_5H_4)\}_2SiMe_2$ from $SnBu_4$, which is also a product in the reaction, proves to be quite difficult. The separation is made even more intricate by the necessity to deactivate the alumina column prior to use by treatment with ether. The most efficient route to 1 is to use the bis(ferrocenyl) compound contaminated with $SnBu_4$ (~10 mol %, the exact ratio is determined in ^1H NMR spectra). The $SnBu_4$ does not appear to have any deleterious effects on the yield in the final transmetalation step. Monomer 1 is isolated in a 30% overall yield starting from $\{\eta^5\text{-}C_5H_4SnBu_3\}_2Fe$.



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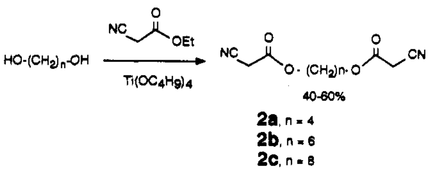
Monomer 1 is isolated as air-stable deep red crystals. Spectroscopic data are consistent with two equivalent ferrocene units linked by the Me_2Si bridge. We have characterized complex 1 by a single-crystal molecular structure study. A drawing of the structure is displayed in Figure 1, and a summary of the crystallographic study is presented in Table I. The molecular structure possesses a C_2 axis of symmetry which bisects the two Si–methyl bonds and goes through the silicon atom. The structure is currently being used to help model these new Me_2Si-bridged bis(ferrocenyl) polymers.

The bis(cyanoacetate) monomers 2 are prepared by reaction of the appropriate diol with an excess of ethyl cyanoacetate in the presence of a catalytic amount of $Ti(OC_4H_9)_4$ (eq 2).[8] At the completion of the reaction the monomers are purified by crystallization from ethyl acetate/hexanes. Monomers **2a–c** are white crystalline



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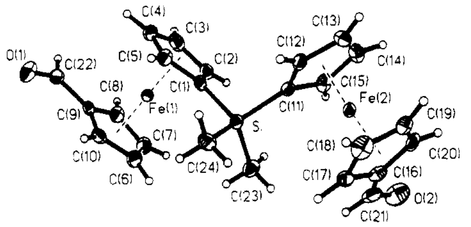


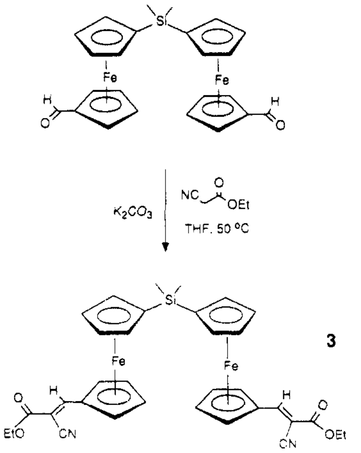
Figure 1. Drawing of $\{(\eta^5\text{-}C_5H_4CHO)Fe(\eta^5\text{-}C_5H_4)\}_2SiMe_2$ (1) using 30% probability thermal ellipsoids. The hydrogen atoms are given arbitrarily small thermal parameters for clarity. See Table I for a summary of the crystallographic data.

Table I
Summary of Pertinent Crystallographic Data for the Single-Crystal Molecular Structure Study of $\{(\eta^5\text{-}C_5H_4CHO)Fe(\eta^5\text{-}C_5H_4)\}_2SiMe_2$ (1)

formula	$C_{24}H_{24}Fe_2O_2Si$
fw	484.2
unit cell	a = 7.644 (3) Å b = 9.523 (1) Å c = 28.740 (4) Å V = 2092.1 (8) Å^3
space group	$P2_12_12_1$
D_{calcd}, g/cm^3	1.537
crystal size, mm	0.4 × 0.4 × 0.2
μ (Moα), mm^{-1}	1.460
scan type	2θ–θ
scan speed, deg/min	variable, 3.0–14.65
scan range, 2θ, deg	3.0–50.0
total data	4081
unique data	3705
data with $F_o > 3.0\sigma(F)$	3413
no. of params refined	263
R, %	5.13
R_w, %	5.48
GOF	1.58

materials which can be stored at ambient temperature for months without any indication of decomposition.

Complex 1 is reacted with ethyl cyanoacetate to afford monomer 3 (eq 3). Only the E isomer is formed in the reaction. This is consistent with related ferrocene α-cyanoacrylate complexes prepared in our laboratory.[1] The latter have been characterized by extensive spectroscopic and X-ray diffraction data. Complex 3 is isolated after column chromatography as a purple oil which exhibits good air stability, even in solution. Monomer 3 is a suitable comonomer for copolymerization with selected diols under Lewis acid catalysis.



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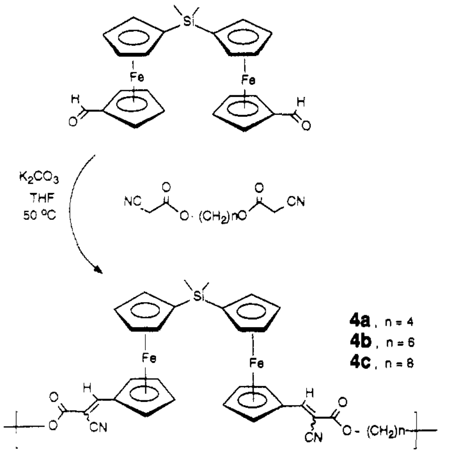
Copolymer Synthesis and Characterization. Our initial strategy to prepare the accordion copolymers was to carry out a polycondensation of monomer 3 with various diols. The transesterification method appears desirable because it is proven to be such a successful method of synthesizing organic main-chain NLO polymers.[9] Monomer 3 is treated with hexanediol in the presence of Ti(OC_4H_9)$_4$ (2 mol %) at 150 °C for 12 h. The product of the reaction is insoluble in organic solvents such as chloroform and dichloromethane. The elemental analysis data are close to those anticipated for the polymeric product; however, the lack of solubility is not consistent with subsequent results that we have obtained.

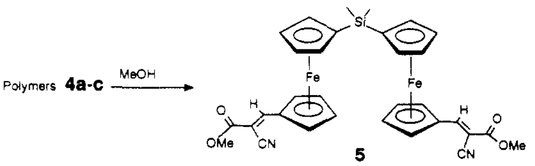
Scheme I



The results above suggest that the reaction conditions required to carry out the Lewis acid catalyzed transesterification polycondensation have deleterious effects on the bis(ferrocenyl) monomer and/or the polymeric product. We then changed our strategy and constructed the polymer backbone through the Knoevenagel condensation reaction. For the ferrocenecarboxaldehydes we find this reaction to proceed in very high yields and that it can be accomplished using very mild reaction temperatures (25–50 °C).[10] This reaction also possesses good functional group tolerance because of the mild base (i.e., K_2CO_3 or DMAP) used. This latter point will become important in future generations of NLO polymers being prepared in our laboratory.

The copolymerization of monomers 1 and 2 is carried out by heating a THF solution to 50 °C in the presence of excess potassium carbonate for 12 h (Scheme I). Spectroscopic analysis of the crude polymer indicates a mixture of E and Z isomers are formed in the polymerization reaction. The E/Z ratio is found to vary in the range of 5–10. When the copolymers are purified by precipitation into methanol, the E isomer is enriched to ~98%. The filtrate contains polymer with a M_n approximately 30% lower than that of the original polymer mixture. The polymer in the filtrate does contain the Z isomer, but not at an enriched level.

In addition to separating out the Z isomers we find that the filtrate from the polymer precipitation experiments contains a new product (eq 4). Spectroscopic and analytical data are consistent with the dimethyl ester structure 5. Complex 5 is isolated in small quantities from the polymerizations utilizing 2a–c. We believe that complex 5 arises through a transesterification/depolymerization process of the accordion main-chain organometallic poly-



(4)

Table II
Molecular Weight Data and Thermal Analysis Data for Polymers 4

polymer	M_n	M_w	T_m or T_g	break point in TGA, °C
4a	9 200	19 000	none	270[a]
4b	9 100	18 200	none	275
4c	26 600	55 000	none	285

[a] Under a nitrogen atmosphere, ramp rate of 10 °C/min. Break point is the temperature where a continuous and rapid weight loss began to occur.

mer. We believe that the *Z* isomer undergoes the depolymerization faster than the *E* isomer.

The accordion main-chain organometallic polymers are soluble in most organic solvents (i.e., benzene, chloroform, dichloromethane, and tetrahydrofuran), and for **4c** we are able to cast free-standing films. Gel permeation chromatography of the polymers shows that comonomer **2c** affords the highest molecular weight polymer (Table II). Films of polymer **4c** are elastic and can be stretched by nearly 100% of their original length before tearing. The lower molecular weight polymers form films which are much more brittle.

Concluding Remarks

In this study we have demonstrated the feasibility of preparing accordion-type organometallic polymers. The key to our success in obtaining the new organometallic polymers is utilization of the Knoevenagel polycondensation technique. The mild reactions conditions overted deleterious side reactions which occur when heating ferrocenyl NLO-phore monomers in the presence of Lewis acids. The transesterification/depolymerization we observe for the accordion polymers indicates that alcoholic solvents should be avoided. Future work in our laboratory will focus on obtaining accordion main-chain organometallic polymers with more elaborate functionality, obtaining higher molecular weight polymers, and evaluation of these new organometallic NLO polymers for second harmonic generation (SHG) activity.

Experimental Section

Methods. All manipulations of compounds and solvents were carried out by using standard Schlenk techniques. Solvents were degassed and purified by distillation under nitrogen from standard drying agents. Spectroscopic measurements utilized the following instrumentation: ^1H NMR, Varian XL 300; ^{13}C NMR, Varian XL 300 (at 75.4 MHz). NMR chemical shifts are reported in δ versus Me_4Si in ^1H NMR and assigning the $CDCl_3$ resonance at 77.00 ppm in ^{13}C spectra. The $\{\eta^5\text{-}C_5H_4SnBu_3\}_2Fe$ was prepared by a modification of the literature method.[3a] The ethyl cyanoacetate (98% purity), $Ti(OC_4H_9)_4$, and the butane-, hexane-, and octanediols were purchased from Aldrich Chemical Co. and used as received. The K_2CO_3 (granular, AR grade, Mallinckrodt) was purchased from Baxter. Polymer analyses were performed using a Perkin-Elmer TGA7 and DSC7 thermal analysis data station. GPC data were collected using a Varian 5000 HPLC using a Polymer Laboratory mixed-gel column (300 × 7.5 mm, 5 μm) at a flow rate of 1.0 mL/min. The column was calibrated using polystyrene standards (1200–500000), and the molecular weights given are relative to these standards. Elemental analyses were performed at Atlantic Microlab Inc., Norcross, GA.

Preparation of $\{(\eta^5\text{-}C_5H_4SnBu_3)Fe(\eta^5\text{-}C_5H_4)\}_2SiMe_2$. A chilled (−78 °C) THF (100 mL) solution containing $(\eta^5\text{-}C_5H_4SnBu_3)_2Fe$ (12.54 g, 16.4 mmol) was treated with 1.0 mol equiv of *n*-BuLi (6.56 mL, 16.4 mmol) and allowed to stir for 30 min and then allowed to warm for 10 min. A solution of THF (10 mL) containing 0.5 mol equiv of $(CH_3)_2SiCl_2$ (0.99 mL, 8.2 mmol) was cannulated into the warming solution. This was allowed to warm to ambient temperature and stirred for 30 min. The mixture was diluted with ether (100 mL) and washed with water (2 × 100 mL) and then brine (100 mL), and the organic layer was dried over K_2CO_3. The solvent was removed under reduced pressure, and the crude product was subjected to column chromatography (4 × 30 cm) on deactivated alumina. Elution with hexanes under nitrogen produced three bands. The first orange band (minor) contained starting material and $SnBu_4$. The second and major orange band was collected, and solvents were removed under reduced pressure to afford reasonably pure $\{(\eta^5\text{-}C_5H_4SnBu_3)Fe(\eta^5\text{-}C_5H_4)\}_2SiMe_2$ (3.5 g, 43%) as an orange oil: ^1H NMR ($CDCl_3$) δ 4.26 (m, 8 H, Cp), 4.09 (t, *J* = 1.7 Hz, 4 H, Cp), 3.96 (t, *J* = 1.6 Hz, 4 H, Cp), 1.57 (m, 12 H, CH_2), 1.38 (m, 12 H, CH_2), 1.04 (m, 12 H, CH_2), 0.94 (t, *J* = 7.3 Hz, 18 H, CH_3), 0.53 (s, 6 H, $SiCH_3$); ^{13}C ($CDCl_3$) δ 74.4 (Cp), 72.9 (Cp), 71.3 (*ipso*-Cp), 70.9 (Cp), 69.0 (*ipso*-Cp), 29.2, 27.4 (CH_2's), 13.7 (CH_3), 10.2 ($SnCH_2$), 0.9 ($SiCH_3$).

Preparation of $\{(\eta^5\text{-}C_5H_4CHO)Fe(\eta^5\text{-}C_5H_4)\}_2SiMe_2$ (1). A chilled (−78 °C) THF (40 mL) solution containing $\{(\eta^5\text{-}C_5H_4SnBu_3)Fe(\eta^5\text{-}C_5H_4)\}_2SiMe_2$ (3.57 g, 3.57 mmol) was treated with 2.0 mol equiv of *n*-BuLi (2.90 mL, 8.14 mmol) and allowed to react for 30 min. *N*,*N*-Dimethylformamide (1.40 mL, 17.9 mmol) was added to the mixture and the cooling bath removed. After 2 h the reaction mixture was diluted with ether (100 mL) and washed with water (2 × 100 mL) and then brine (100 mL), and the organic layer was dried over K_2CO_3. The solvents were removed under reduced pressure, and the crude product was subjected to column chromatography (2.5 × 20 cm) on deactivated alumina. Gradient elution first with ethyl acetate/hexanes (1/3, v/v) and then ending with chloroform was utilized. The second (major) red/orange band was collected, and the solvents were removed under reduced pressure to afford pure $\{(\eta^5\text{-}C_5H_4CHO)Fe(\eta^5\text{-}C_5H_4)\}_2SiMe_2$ (**1**) (1.18 g, 68.0%, mp 127–128 °C): ^1H NMR ($CDCl_3$) δ 9.86 (s, 2 H, CHO), 4.71 (t, *J* = 2.0 Hz, 4 H, Cp), 4.48 (m, 8 H, Cp), 4.17 (t, *J* = 2.0 Hz, 4 H, Cp), 0.50 (s, 6 H, $SiCH_3$); ^{13}C ($CDCl_3$) δ 193.3 (CHO), 79.2 (*ipso*-Cp), 74.4 (Cp), 73.3 (Cp), 73.2 (*ipso*-Cp), 72.5 (Cp), 69.8 (Cp), 1.4 ($SiCH_3$). Anal. Calcd for $C_{24}H_{24}Fe_2O_2Si$: C, 59.53; H, 5.00. Found: C, 59.90; H, 4.96.

X-ray Diffraction Study of Complex 1. Crystals of **1** were grown through slow diffusion of pentane into a chloroform solution of complex **1**. Crystals were mounted on glass fibers and secured by epoxy cement. Unit cells were determined through centering on at least 15 reflections with 2θ greater than 15°. Intensity data were collected on a Siemens P4 diffractometer. The structure solution (direct methods) and refinement was accomplished using the SHELXTL PLUS package of programs. All non-hydrogen atoms were refined anisotropically, and hydrogen atoms were refined in an idealized geometry (riding model, 0.95 Å) with set isotropic thermal parameters. See Table I for a summary of pertinent facts concerning the crystal, data collection, and details of the refinement process used in the structure determination.

Preparation of $CNCH_2CO_2(CH_2)_6O_2CCH_2CN$ (2b). A Schlenk flask was charged with $CNCH_2CO_2Et$ (10.0 g, 88.4 mmol), 1,6-hexanediol (5.22 g, 44.2 mmol), and $Ti(OC_4H_9)_4$ (0.45 g, 0.30 mL, 1.5 mol %). The mixture was heated in an oil bath at 100 °C for 12 h under a slow stream of nitrogen in order to purge the ethanol from the reaction vessel. The mixture was allowed to cool and filtered through a pad (4 × 7 cm) of deactivated alumina. The alumina was washed with chloroform (150 mL), and the solvents were removed from the filtrate under reduced pressure. The crude product was recrystallized from hot hexanes and ethyl acetate (1/1, v/v). The white crystalline solid was collected and dried under reduced pressure to afford 10.0 g (90%) of $CNCH_2CO_2(CH_2)_6O_2CCH_2CN$ (**2b**).

$CNCH_2CO_2(CH_2)_4O_2CCH_2CN$ (2a): 88%; mp 43–44 °C; ^1H NMR ($CDCl_3$) δ 4.22–4.27 (m, 4 H, CH_2O), 3.46 (s, 4 H, CH_2CN), 1.77–1.81 (m, 4 H, CH_2); ^{13}C ($CDCl_3$) δ 162.9 (CO_2), 113.1 (CN), 65.9 (CH_2O), 24.63, 24.57 (CH_2's). Anal. Calcd for $C_{10}H_{12}N_2O_4$: C, 53.57; H, 5.40. Found: C, 53.42; H, 5.32.

$CNCH_2CO_2(CH_2)_6O_2CCH_2CN$ (2b): 90%; mp 69–70 °C; ^1H NMR ($CDCl_3$) δ 4.20 (t, *J* = 6.6, 4 H, CH_2O), 3.45 (s, 4 H, CH_2CN), 1.69 (m, 4 H, CH_2), 1.41 (m, 4 H, CH_2); ^{13}C NMR ($CDCl_3$) δ 162.9 (CO_2), 113.0 (CN), 66.7 (CH_2O), 28.1, 25.3, 24.7 (CH_2's).

$CNCH_2CO_2(CH_2)_8O_2CCH_2CN$ (2c): 85%; mp 48–49 °C; ^1H NMR ($CDCl_3$) δ 4.19 (t, *J* = 6.6, 4 H, CH_2O), 3.44 (s, 4 H, CH_2CN), 1.64–1.67 (m, 4 H, CH_2), 1.25–1.35 (m, 8 H, CH_2); ^{13}C NMR

($CDCl_3$) δ 162.9 (CO_2), 113.1 (CN), 66.9 (CH_2O), 28.8, 28.2, 25.5, 24.7 (CH_2's). Anal. Calcd for $C_{14}H_{20}N_2O_4$: C, 59.99; H, 7.19. Found: C, 60.20; H, 7.25.

Preparation of 3. A THF (10 mL) solution of 1 (0.32 g, 0.66 mmol), ethyl cyanoacetate (0.19 g, 1.7 mmol), and K_2CO_3 (1.5 g) was heated at 50 °C with stirring for 16 h. The mixture was diluted with ether (100 mL), washed with water and then brine, and finally dried over K_2CO_3. The solvents were removed under reduced pressure, and the crude product was subjected to column chromatography on alumina. Elution with ethyl acetate/hexanes (1/9, v/v) afforded a purple band which was collected, and the solvent was removed to afford pure **3** (0.42 g, 94%): ^1H NMR ($CDCl_3$) δ 8.08 (s, 2 H, CH=), 4.92 (t, *J* = 1.9 Hz, 4 H, Cp), 4.59 (t, *J* = 1.9 Hz, 4 H, Cp), 4.48 (t, *J* = 1.8 Hz, 4 H, Cp), 4.31 (q, *J* = 7.1 Hz, 4 H, OCH_2), 4.14 (t, *J* = 1.7 Hz, 4 H, Cp), 1.37 (t, *J* = 7.1 Hz, 6 H, CH_2CH_3), 0.49 (s, 6 H, $SiCH_3$); ^{13}C NMR ($CDCl_3$) δ 163.1 (CO_2), 158.3 (=*C*H), 116.8 (CN), 97.7 (=*C*(CN)), 75.2 (Cp CH), 74.3 (Cp CH), 74.2 (*ipso*-Cp), 73.9 (Cp CH), 73.5 (*ipso*-Cp), 71.8 (Cp CH), 62.1 (OCH_2), 14.2 (CH_2CH_3), −1.4 ($SiCH_3$); IR (CH_2Cl_2) ν_{CN} 2224, $\nu_{C=O}$ 1716, and $\nu_{C=C}$ 1598 cm^{-1}. Anal. Calcd for $C_{34}H_{34}Fe_2N_2O_4Si$: C, 60.56; H, 5.08. Found: C, 60.26; H, 5.20.

Preparation of Copolymer 4. A solution of THF (4 mL) containing $\{(\eta^5\text{-}C_5H_4CHO)Fe(\eta^5\text{-}C_5H_4)\}_2SiMe_2$ (0.200 g, 0.413 mmol), $CNCH_2CO_2(CH_2)_6O_2CCH_2CN$ (0.104 g, 0.413 mmol), and K_2CO_3 (0.35 g, 0.62 mmol) was heated at 50 °C for period of 12 h. The mixture was filtered through Celite, and the solvents were removed under reduced pressure. The crude product was dissolved in chloroform and precipitated in methanol. The copolymer was collected and washed with cold methanol (3 × 25 mL) and then dried under reduced pressure at 65 °C for 24 h.

Copolymer 4a: ^1H NMR ($CDCl_3$) δ 8.09 (s, 2 H, =CH) 4.93 (t, *J* = 1.9 Hz, 4 H, Cp), 4.60 (t, *J* = 1.9 Hz, 4 H, Cp), 4.49 (t, *J* = 1.7 Hz, 4 H, Cp), 4.32 (m, 4 H, CH_2O), 4.15 (t, *J* = 1.7 Hz, 4 H, Cp), 1.9 (m, 4 H, CH_2), 0.49 (s, 6 H, $SiCH_3$); ^{13}C ($CDCl_3$) δ 163.1 (CO_2), 158.6 (=*C*H), 116.7 (CN), 97.4 (=*C*(CN)), 75.2 (Cp CH), 74.4 (Cp CH), 74.2 (*ipso*-Cp CH), 74.0 (Cp CH), 73.6 (*ipso*-Cp), 71.9 (Cp CH), 65.4 (CH_2O), 25.2 (CH_2), −1.4 ($SiCH_3$). Anal. Calcd for $\{C_{34}H_{32}Fe_2N_2O_4Si\}_n$: C, 60.73; H, 4.80. Found: C, 60.24; H, 4.75.

Copolymer 4b. Major isomer: ^1H ($CDCl_3$) δ 8.08 (s, 2 H, =CH), 4.92 (t, *J* = 1.9 Hz, 4 H, Cp), 4.59 (t, *J* = 1.9 Hz, 4 H, Cp), 4.49 (t, *J* = 1.7 Hz, 4 H, Cp), 4.26 (t, *J* = 6.6 Hz, 4 H, OCH_2), 4.14 (t, *J* = 1.7, 4 H, Cp), 1.76–1.78 (m, 4 H, CH_2), 1.48–1.51 (m, 4 H, CH_2), 0.53 (s, 6 H, $SiCH_3$); ^{13}C ($CDCl_3$) δ 163.1 (CO_2), 158.4 (=*C*H), 116.7 (CN), 97.6 (=*C*(CN)), 75.2 (Cp CH), 74.3 (Cp CH), 74.2 (*ipso*-Cp), 74.0 (Cp CH), 75.5 (*ipso*-Cp), 71.9 (Cp CH), 66.0 (OCH_2), 28.4, 25.5 (CH_2's), −1.4 ($SiCH_3$).

Minor isomer: ^1H ($CDCl_3$) δ 8.07 (s, 2 H), 4.92 (t, *J* = 1.9 Hz, 4 H, Cp), 4.60 (t, *J* = 1.9 Hz, 4 H, Cp), 4.47 (t, *J* = 1.7 Hz, 4 H, Cp), 4.32 (t, *J* = 6.6 Hz, 4 H, CH_2O), 4.11 (t, *J* = 1.7, 4 H, Cp), 1.76–1.78 (m, 4 H, CH_2), 1.48–1.51 (m, 4 H, CH_2), 0.49 (s, 6 H, $SiCH_3$). Anal. Calcd for $\{C_{36}H_{36}Fe_2N_2O_4Si\}_n$: C, 61.73; H, 5.18. Found: C, 61.00; H, 5.22.

Copolymer 4c: ^1H ($CDCl_3$) δ 8.08 (s, 2 H), 4.92 (t, *J* = 1.9 Hz, 4 H, Cp), 4.59 (t, *J* = 1.9 Hz, 4 H, Cp), 4.49 (t, *J* = 1.7 Hz, 4 H, Cp), 4.25 (t, *J* = 6.5 Hz, 4 H, CH_2O), 4.14 (t, *J* = 1.7 Hz, 4 H), 1.72 (m, 4 H, CH_2), 1.39 (m, 8 H, CH_2), 0.49 (s, 6 H, $SiCH_3$); ^{13}C NMR ($CDCl_3$) δ 163.1 (CO_2), 158.3 (=*C*H), 116.7 (CN), 97.6 (=*C*(CN)), 75.1 (Cp CH), 74.2 (Cp CH), 74.16 (*ipso*-Cp CH), 73.9 (Cp CH), 73.5 (*ipso*-Cp), 71.8 (Cp CH), 66.1 (OCH_2), 29.0, 28.4, 25.7 (CH_2's), −1.4 ($SiCH_3$); IR (CH_2Cl_2) ν_{CN} 2222, $\nu_{C=O}$ 1718, and $\nu_{C=C}$ 1593 cm^{-1}. Anal. Calcd for $\{C_{38}H_{40}Fe_2N_2O_4Si\}_n$: C, 62.05; H, 5.53; N, 3.84. Found: C, 61.70; H, 5.44; N, 3.76.

Characterization of Complex 5. Spectroscopic data: ^1H NMR ($CDCl_3$) δ 8.09 (s, 2 H, =CH), 4.93 (t, *J* = 1.8 Hz, 4 H, Cp), 4.61 (t, *J* = 1.8 Hz, 4 H, Cp), 4.49 (t, *J* = 1.8 Hz, 4 H, Cp), 4.14 (t, *J* = 1.7 Hz, 4 H, Cp), 3.87 (s, 6 H, OCH_3), 0.49 (s, 6 H, $SiCH_3$); ^{13}C NMR ($CDCl_3$) δ 163.0 (CO_2), 158.3 (=*C*H), 116.7 (CN), 97.6 (=*C*(CN)), 75.1 (Cp CH), 74.2 (Cp CH), 74.16 (*ipso*-Cp CH), 73.9 (Cp CH), 73.5 (*ipso*-Cp), 71.8 (Cp CH), 55.8 (OCH_3), −1.4 ($SiCH_3$); IR (CH_2Cl_2) ν_{CN} 2220, $\nu_{C=O}$ 1720, and $\nu_{C=C}$ 1595 cm^{-1}. Anal. Calcd for $C_{32}H_{30}Fe_2N_2O_4Si$: C, 59.47; H, 4.68. Found: C, 59.30; H, 4.53.

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Supplementary Material Available: Tables of structure determination summary, atomic coordinates, bond lengths, bond angles, anisotropic displacement coefficients, and hydrogen atom coordinates for 1 (10 pages). Ordering information is given on any current masthead page.

References and Notes

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Registry No. 1, 142840-89-9; **2a**, 42270-85-9; **2b**, 75750-46-8; **2c**, 142723-44-2; **3**, 142840-87-7; **4a** (copolymer), 142840-90-2; **4b** (copolymer), 142840-91-3; **4c** (copolymer), 142840-92-4; **5**, 142840-93-5; $(\eta^5\text{-}C_5H_4SnBu_3)_2Fe$, 12291-11-1; $(CH_3)_2SiCl_2$, 75-78-5; $[(\eta^5\text{-}C_5H_4SnBu_3)Fe(\eta^5\text{-}C_5H_4)]_2SiMe_2$, 142840-94-6; $Me_2NC(O)H$, 68-12-2; $CNCH_2CO_2Et$, 105-56-6; $HO(CH_2)_6OH$, 629-11-8; **3**/1,6-hexanediol (copolymer), 142840-88-8.