Poly(ferrocenylenevinylene) from Ring-Opening Metathesis Polymerization of *ansa*-(Vinylene)ferrocene

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*Summary: The vinylene-bridged ansa-ferrocene complex $[(\eta^5-C_5H_4)CH{=}CH(\eta^5-C_5H_4)]Fe$ (**1**) was synthesized by the McMurry coupling of 1,1'-ferrocenedicarbaldehyde (**2**). The ring opening metathesis polymerization (ROMP) of this strained metallocene gave poly(ferrocenylenevinylene) (**3**) as an insoluble orange solid which has a conductivity of $10^{-3}\,\Omega^{-1}\,cm^{-1}$ after doping with iodine. Partially soluble materials resulted when **1** was copolymerized with norbornene to yield a block copolymer.*

Introduction

Conjugated and electroactive polymers have been the subject of increasing research interest in recent years.[1] Work in this area has shown that these materials may possess interesting properties such as conductivity,[1a−f] electroluminescence,[1g−i] and ferromagnetism,[1j] which make them potentially useful in the fabrication of various semiconductor-based devices.[1k−m] The range of properties available from electron-delocalized polymers could likely be increased by the presence of transition metal centers in the main chain, which could function as coordination sites for analyte molecules in a sensor application[2] or as redox centers for selective and reversible doping of the polymer.[3] Redox-active materials have been synthesized by incorporation of transition metal complexes such as ferrocene into macromolecular structures.[4] However, the vast majority of these contain pendant ferrocenyl groups, are usually nonconducting, and exhibit electrochemical behavior similar to that of ferrocene itself.[5,6] Hybrid polymeric structures possess-ing both inherent electron delocalization and redox active centers along the backbone represent new materials in which the organic portions of the structure may facilitate electronic interactions between the metal centers.[7]

We have been exploring routes to metal-containing, conjugated polymers, which place the metal redox center directly in the polymer's conduction path to maximize its contribution to the material's electronic properties. Poly(phenylenevinylene) (PPV) is one of the most thoroughly investigated conjugated organic polymers, due to its high conductivity and luminescent properties.[1] We report here the synthesis of an organometallic analog to PPV, poly(ferrocenylenevinylene) (PFV), via the ring-opening metathesis polymerization (ROMP) of a vinylene-bridged *ansa*-ferrocene complex. Studies carried out on short polyene segments substituted at both ends with ferrocene provide evidence of strong electronic coupling between the two metal centers.[8] Interesting reports have appeared on electron-delocalized polymers containing ferrocenylene groups linked by ER_2 (E = Si, Ge, and Sn),[9] chalcogen,[10] aromatic,[11] and 1,3-butadienyl[12] groups. Polymers with directly linked ferroce-

[⊗] Abstract published in *Advanced ACS Abstracts,* March 1, 1997.
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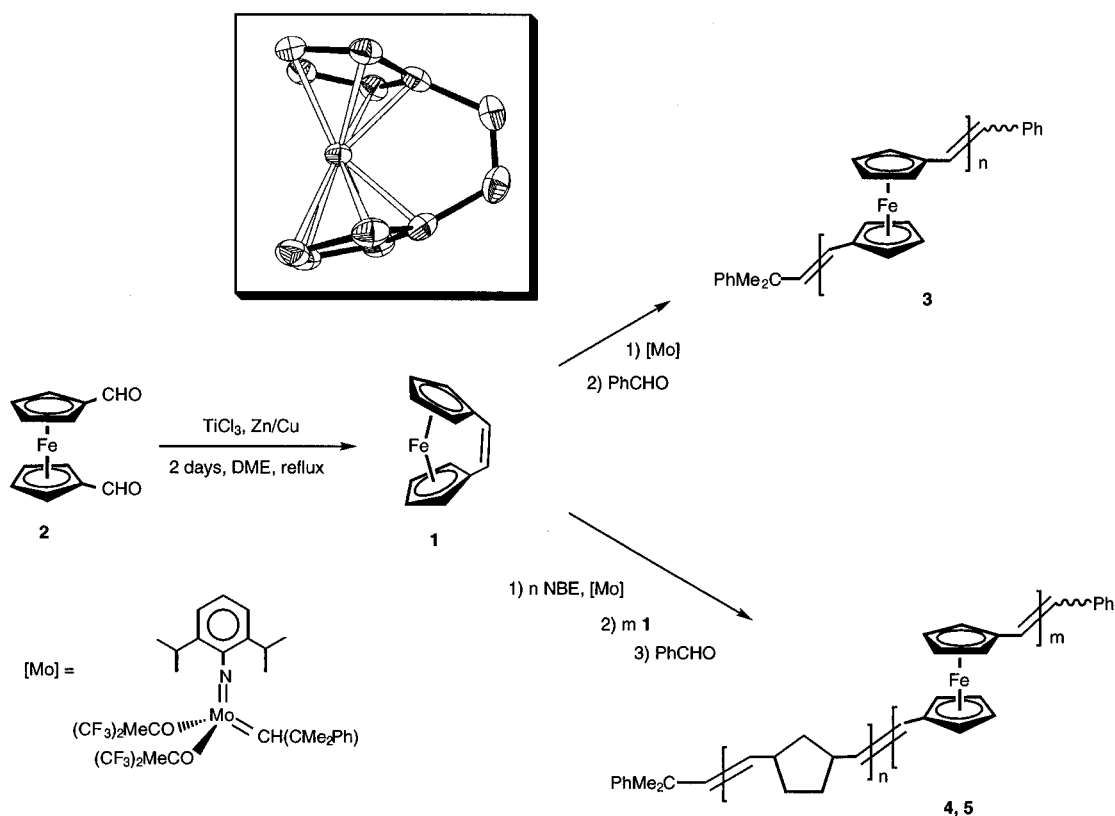(3) Wrighton, M. S. *Comments Inorg. Chem.* **1985,** *4,* 269.
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Scheme 1

nylene groups have also been described.[13] A previous attempt to synthesize PFV using the ADMET polymerization of 1,1'-divinylferrocene yielded $[-C_5H_4FeC_5H_4CH=CH-]_n$ oligomers with an average of 4 repeat units.[14] Recently, alkyl-substituted poly(ferrocenylenevinylene)s have been obtained via the reductive-coupling of $(\eta^5\text{-}1\text{-alkyl-}3\text{-CHO-}C_5H_3)_2Fe$ and $(\eta^5\text{-}C_5H_4\text{-}COMe)_2Fe$ monomers.[15] We reasoned that the living ROMP[16] of suitable monomers such as **1** (Scheme 1) might provide a general and versatile pathway to PFV and its derivatives by allowing more control over molecular weight, endgoup choice, and copolymer formation.

Results and Discussion

The ROMP synthesis of PFV required the *ansa*-(vinylene)ferrocene monomer (**1**), which was previously unknown. This complex was synthesized by the intramolecular McMurry coupling[17] of 1,1'-ferrocenedicarbaldehyde[18] (**2**, Scheme 1). A solution of **2** was slowly added to the McMurry reagent via syringe pump over

2 days to maintain a very low concentration of **2**. The high dilution is essential for the formation of **1**, since at higher dicarbaldehyde concentrations intermolecular coupling predominates.[19] After chromatography and sublimation, the product was isolated in variable yield (0–44%) as air-stable red crystals. Despite use of McMurry's optimized procedure[17c] and our own attempts to maximize the yield, this variability could not be effectively controlled. Even in cases where little or no **1** was isolated, **2** was completely consumed to produce high yields of $[-C_5H_4FeC_5H_4CH=CH-]_n$ oligomers.[19] An X-ray structure determination[20] revealed a "bent-sandwich" geometry for **1**, with the Cp least-squares planes intersecting at an angle of 23°. This value reflects moderate ring strain and is similar to those found in other *ansa*-ferrocene compounds known to undergo thermal ring-opening polymerization.[21] Distortion in the metallocene is evidenced by a displacement of the *ansa*-substituted ring carbons out of the plane defined by their related ring atoms and toward the Fe atom. However, the CH=CH—C angle is 117.8(3)° and the CH=CH distance is 1.315(5) Å, indicating that the geometry of the double-bond bridge is not appreciably distorted. The ^1H NMR and visible spectra of *ansa*-metallocenes can be used as qualitative indications of ring strain.[22] Thus, the chemical shift difference between the Cp ring H_α and H_β resonances is remark-

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ably high for *ansa*-metallocenes (0.79 ppm for **1**), indicating significant strain. For 1,1′-divinylferrocene, the closest nonbridged analog to **1**, this value is 0.18 ppm.[9g,23] The λ_{max} values for *ansa*-ferrocenes have been shown to undergo a bathochromic shift which increases in magnitude with greater degrees of Cp-ring tilt.[9g,23] Compound **1** is red in solution and displays a λ_{max} value of 470 nm, which is red-shifted with respect to that of ferrocene (λ_{max} 440 nm). The electrochemical properties of **1** in CH_2Cl_2 are very similar to those of ferrocene; thus a reversible one-electron redox wave with $E_{1/2} = 237$ mV is observed for **1**. In acetonitrile, the oxidation was found to be irreversible, as evidenced by the absence of a cathodic wave.

In the presence of the ROMP catalyst Mo[N(2,6-^{i}Pr$_2$C$_6$H$_3$)](CHCMe$_2$Ph)[OCMe(CF$_3$)$_2$]$_2$,[24] **1** polymerizes slowly in benzene solution at room temperature with complete consumption of the monomer after 10 h to give an orange precipitate (**3**). This material is completely insoluble in organic solvents such as toluene, THF, CH_2Cl_2, DMF, DMSO, and *N*-methylpyrrolidone. X-ray powder diffraction measurements on a pressed sample revealed only one very broad scattering maximum at $2\theta = 16.5°$, indicating that **3** is slightly crystalline. Thermogravimetric analysis showed that the polymer is stable up to 300 °C under a N_2 atmosphere and decomposes with a one-step mass loss to a black residue (char yield: 52%). The infrared spectrum of **3** contains a single broad C=C−H stretching vibration at 3081 cm^{-1} but two C−H bending modes at 931 and 950 cm^{-1}, assigned to *cis* and *trans* olefinic moieties, respectively.[15,19] A pressed pellet of this material was briefly exposed to I_2 vapor (ca. 1 min) under reduced pressure, resulting in a color change from orange to metallic gray. The conductivity of the pellet under a nitrogen atmosphere was found to be 1×10^{-3} Ω^{-1} cm^{-1} by the in-line four point probe method. This value is intermediate between values reported for $[-(\eta^5$-C$_5$H$_4$)Fe$(\eta^5$-C$_5$H$_4$)-CH=CHCH=CH−]_n$ $(1 \times 10^{-4}$ Ω^{-1} cm^{-1})[12] and $\{-[\eta^5$-C$_5$H$_3$(C$_6$H$_{13}$)]Fe$[\eta^5$-C$_5$H$_3$(C$_6$H$_{13}$)]CH=CH−\}_n$ $(1 \times 10^{-2}$ Ω^{-1} cm^{-1}).[15a]

Block copolymers of **1** with norbornene (NBE) were found to have moderate solubility in organic solvents. A benzene solution of norbornene was treated with the molybdenum ROMP catalyst in order to form living oligomers. To these, **1** was added and the polymerization continued, giving a cloudy red solution. After solvent removal a thick red gel (**4**) remained, which could be partially redissolved in benzene, THF, and CH_2Cl_2. A material prepared with a catalyst:NBE:**1** ratio of 1:10:10 revealed resonances attributable to poly(NBE) and the Cp protons. Two sets of vinylic proton signals were observed for the (NBE)$_n$ block (δ 5.51, br s, 12% *trans*; δ 5.35, br s, 88% *cis*) and the (**1**)$_m$ block (δ 6.44, br m, 33% trans; δ 6.21, br m, 67% *cis*). In related polymerizations, it has been shown by Schrock et al. that the molybdenum catalyst usually gives both *cis* and *trans* metathesis products.[25] Repeated washing of the THF-soluble fraction of this copolymer by precipitation in pentane removed little or no poly(NBE), indicating that the material is a diblock

and not a mixture of two homopolymers. Gel permeation chromatography (GPC) gave $M_w/M_n = 1710/1490$ versus polystyrene standards; however an end-group analysis by ^{1}H NMR spectroscopy on the benzene-soluble fraction of **4** gave $M_n =$ ca. 3000. Use of a catalyst:NBE:**1** ratio of 1:50:10 also gave a partially soluble material (**5**) which has a higher molecular mass ($M_w/M_n = 21000/11000$ by GPC) and is spectroscopically very similar to copolymer **4**. The relatively broad molecular weight distribution suggests that the polymerization is not entirely living and is also consistent with the fact that insoluble polymer (typically ca. 20%) forms early in the course of monomer consumption.

Electrochemical methods were used to probe interactions between the iron centers in the poly(ferrocenylenevinylene) block. The cyclic voltammagram shows two reversible redox waves with a separation of 250 mV. The two-wave pattern is characteristic of a chain of interacting centers,[26,9h,i] whereas a single wave would be expected for a chain of noninteracting centers.[27] The separation between the two redox potentials (ΔE) is roughly indicative of the magnitude of the interaction. For comparison, the $[-C_5H_4FeC_5H_4SiR_2-]_n$ polymers reported by Manners have ΔE values of 210−290 mV,[9g] and the $[-(C_5H_3^tBu)Fe(C_5H_3^tBu)S]_n$ polymer prepared by Rauchfuss exhibits a ΔE value of 290 mV.[10a]

We conclude that the ROMP of strained, vinylene-bridged ferrocene complexes should offer a general route to conjugated organometallic polymers with metals in the main chain. The material obtained here exhibited weak conductivity when doped with I_2. We are currently investigating improved routes to monomer **1** and related derivatives which might undergo ring-opening metathesis polymerization to metal-containing polymers.

Experimental Section

General Details. All reactions were carried out under a nitrogen atmosphere using standard Schlenk techniques and dry, oxygen-free solvents. Benzene used for ROMP was distilled from Na/K, and 1,2-dimethoxyethane (DME) was distilled from K under nitrogen. Norbornene (NBE) was purchased from Aldrich, sublimed, and then distilled from Na under nitrogen before use. All air-sensitive compounds were handled in a Vacuum Atmospheres drybox with a nitrogen atmosphere. The compound 1,1′-ferrocenedicarbaldehyde[18] and the ROMP catalyst Mo(NAr)(CHC(CH$_3$)$_2$Ph)(OR′)$_2$, where Ar = 2,6-diisopropylphenyl and R′ = CMe(CF$_3$)$_2$[24] were prepared by known procedures.

Elemental analyses were performed at the microanalytical laboratory at the University of California, Berkeley, CA. NMR spectra were obtained in benzene-d_6 obtained from Cambridge Isotope Laboratories and used as received. All NMR spectra were recorded with a Bruker AMX-300 or AMX-400 instrument at room temperature. Chemical shifts are reported in parts per million downfield from tetramethylsilane and are referenced to the residual proton signal or carbon signal of the deuterated solvent. Infrared spectra were obtained using a Mattson FTIR spectrometer. Gel permeation chromatography was performed on a Waters HPLC apparatus with a polystyrene column and a refractometer detector. All samples were dissolved in dry THF, and toluene was used as an internal standard and flow rate marker. Measurements

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obtained by GPC are relative to polystyrene standards. Low-resolution mass spectra were obtained by electron impact ionization at the Mass Spectrometry Facility at the University of California, Berkeley, CA. Powder diffraction patterns were obtained with a Phillips PW1720 X-ray diffractometer at 24 °C using Cu Kα radiation. Thermal analyses were obtained using a Du Pont Model 2000 TGA system under a nitrogen atmosphere. Acetonitrile and CH_2Cl_2 used for electrochemistry were distilled from CaH_2 under N_2 prior to use. Solutions were prepared in the glovebox and analyzed under N_2. Electrochemical measurements were recorded using a BAS 100 potentiostat at a scan rate of 1000 mV s^{-1}. The $E_{1/2}$ value reported is relative to Ag/Ag$^+$. A Ag/AgNO$_3$ (0.01 M AgNO$_3$ in MeCN) reference electrode was used with Pt working and counter electrodes and 0.1 M tetrabutylammonium hexafluorophosphate in CH_2Cl_2 as supporting electrolyte. The analyte concentrations used were approximately 0.01 M.

***ansa*-(Vinylene)ferrocene (1).** A 250 mL round-bottom Schlenk flask equipped with a magnetic stir bar was charged with TiCl$_3$ (3.50 g, 22.7 mmol, 11 equiv), Zn/Cu alloy (3.42 g, 5.16 mmol, 25 equiv), and ca. 80 mL of 1,2-dimethoxyethane. The blue-green suspension was heated at reflux for 1.5 h to give a green-brown slurry. 1,1′-Ferrocenedicarbaldehyde (0.50 g, 2.06, mmol, 1 equiv) dissolved in 10 mL of 1,2-dimethoxyethane was added via a gastight syringe through a septum at the top of the condenser. The syringe was driven by a mechanical syringe pump that delivered the solution at a rate of 0.49 mL/h (0.2 mmol/h). The suspension of coupling reagent was kept at reflux during addition (20 h) and for 10 h after the addition was over. The red-brown suspension was allowed to cool and was filtered through a pad of 200−400 mesh fluorisil to remove the coupling reagent and give an orange-red solution. The 1,2-dimethoxyethane was removed by vacuum transfer, and the crude product was sublimed in vacuo at 45 °C to give **2** (0.192 g, 0.91 mmol, 44%) as a bright red crystalline powder. ^{1}H NMR (400 MHz, C$_6$D$_6$): δ 6.09 (s, 2 H), 4.66 (t, 4 H, $J = 1.6$ Hz), 3.67 (t, 4 H, $J = 1.6$ Hz). ^{13}C{^{1}H} NMR (100 MHz, C$_6$D$_6$): δ 135.9 (CH=CH), 89.5 (*ipso*), 75.3 (C$_\alpha$), 67.9 (C$_\beta$). Anal. Calcd for C$_{12}$H$_{10}$Fe: C, 68.62; H, 4.80. Found: C, 68.16; H, 4.99. IR (KBr pellet): 3088, 3072, 3001, 1369, 1198, 1034, 1022, 920, 858, 845, 823, 795, 761, 660, 532, 509, 432 cm^{-1}. EIMS: *m/z* 210 (M$^+$).

Poly(ferrocenylenevinylene). In the drybox, **1** (0.10 g, 0.476 mmol, 20 equiv) was added to a vial and dissolved in 2 mL of dry benzene. A solution of the molybdenum ROMP catalyst in 1.0 mL of benzene (0.018 g, 0.0238 mmol, 1 equiv) was added rapidly to the solution of **1** and shaken. The red solution darkened during the first 1 h, and the polymer began to precipitate. After 16 h the catalyst was quenched with excess benzaldehyde and the benzene was removed under reduced pressure to give a fluffy insoluble orange powder (0.099 g, 94%). Anal. Calcd for C$_{10}$H$_{12}$(C$_{12}$H$_{10}$Fe)$_{20}$C$_7$H$_6$: C, 69.78; H, 4.97. Found: C, 68.70; H, 4.95. IR (KBr pellet): 3081, 2960, 1239, 1173, 1042, 1025, 950, 931, 823, 757, 519, 485 cm^{-1}.

[Poly(norbornylene)]-block-[poly(ferrocenylenevinylene)]. In the drybox, a Schlenk tube was charged with NBE (0.022 g, 0.223 mmol, 12 equiv). On the Schlenk line, 2.0 mL of dry THF was added to give a clear solution. To this stirred solution was added the molybdenum ROMP catalyst (0.014 g, 0.0186 mmol, 1 equiv), dissolved in 1.0 mL of THF. After 2 min a solution of **1** (0.039 g, 0.186 mmol, 10 equiv) in 1.0 mL of THF was added rapidly and the resulting red mixture was stirred at room temperature for 2 days. An orange-red precipitate formed as the reaction proceeded. The reaction was quenched by addition of an excess of benzaldehyde (0.1 mL), and the volatile material was then removed under vacuum to give a red-brown solid (0.059g, 97%). Addition of THF (2.0 mL) resulted in dissolution of some of the material to give a red-orange solution. After filtration, this solution was poured into pentane (ca. 5 mL) and the resulting mixture was centrifuged to separate the insoluble material. This fractionation procedure was repeated twice more to remove a small amount of poly(NBE), the identity of which was confirmed by ^{1}H NMR spectroscopy. Removal of solvent gave a red-orange glassy solid (0.015 g, 25%). The solublity and molecular weight of this material were oberved to vary slightly from run to run. Fractionation procedures were sometimes frustrated by the occasional tendency of this material to form insoluble gels after a few hours in THF, benzene or dichloromethane. $M_w/M_n = 1560/1490$. ^{1}H NMR (400 MHz, CD$_2$Cl$_2$): δ 7.4−7.1 (br m, 10 H), 6.4−6.0 (br m, 16 H), 5.2 (br s, 10 H), 4.4−4.0 (br m, 53 H), 3.8−3.3 (br s, 23 H), 2.9−2.7 (br s, 12 H), 2.4 (br s, 6 H), 1.9−1.7 (br m, 24 H), 1.5−1.2 (br m, 38 H), 1.1−0.8 (br m, 16 H).

Note Added in Proof. While this paper was being reviewed, an alternative synthetic procedure for **1** was reported: Aggarwal, V. K.; Jones, D.; Turner, M. L.; Adams, H. *J. Organomet. Chem.* **1996**, *524*, 263.