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The Synthesis and Properties of Face-to-Face Metallocene Polymers

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ABSTRACT: Polymerization of 1,1′-bis(8-cyclopentadienyl-1-naphthyl)ferrocene (**8**) and its alkylated analogs **13a**−**d**, through base-assisted, metal complexation, gives a new class of metallocene polymer **14** in which contiguous metallocene rings are held in a stacked, face-to-face orientation. The monomers are prepared in three steps from 1,8-diiodonaphthalene (**2**) through coupling with cyclopentadienylcopper reagents to give 1-cyclopentadienyl-8-iodonaphthalenes **4** or **11**, conversion to the ferrocene derivative by metal complexation with ferrous chloride, and then cyclopentadienylation. Polymers incorporating only ferrocene units as well as copolymers of ferrocene and nickelocene or cobaltocene, in which the metallocenes alternate within the chain, have been prepared. These have been characterized by GPC analysis and by their infrared and ^{1}H NMR spectra. Polymerization of 1,8-bis(cyclopentadienyl)-naphthalene (**15**) and its alkylated derivative **17** by base-assisted complexation provides a new pathway to a broader range of metallocene polymers. These monomers have been polymerized through base-assisted metal complexation with nickel(II) salts to gives low molecular weight, stacked nickelocene polymers. Electrical conductivity of compressed pellets of the ferrocene polymer **14b**, which is less than 10^{-12} S cm^{-1} for the unoxidized material, is greatly increased on oxidative doping with iodine, and reaches a maximum of 6.7×10^{-3} at a nominal oxidation level of 37%. The conductivity data are best accounted for in terms of a phonon-assisted electron-hopping mechanism between Fe(II) and Fe(III) centers. The behavior of the doped ferrocene polymer as a weakly interacting mixed-valence system is supported by Mössbauer spectra of oxidized polymer, which show trapped valence states over a broad temperature range and slow paramagnetic relaxation for the Fe(III) sites at lower temperatures. Bulk susceptibility measurement of paramagnetic polymers shows room temperature magnetic moments for the iron−cobalt copolymer **14i** of 5.2 μ_B and for the nickel polymer **18** of 5.3 μ_B. These values are significantly larger than the moments of either cobaltocene or nickelocene.

Introduction

The synthesis and properties of low-dimensional linear systems, composed of stacked planar organometallic units, are a focus of increasing research interest owing to the potential application of such macromolecules as advanced materials.[1] Apart from those systems in which stacking is the consequence of self-assembly in the condensed phase,[2] there now exists a large and increasing number of *oligomeric* stacked organometallic arrays in which strong covalent bonds between the planar coordinating elements constitute the primary structure-determining element. These encompass several broadly distinguishable forms (Figure 1), among them systems (a) in which aromatic carbocyclic or heterocyclic rings are bifacially complexed to a transition metal[3] as well as a number of stacked complexes (b) incorporating two monofacially complexed aromatic ligands within a cyclophane bridging element.[4] Also included in this family of complexes are those in which successive metal-ring bonding is laterally displaced on either a rigid[5] (c) or a more flexible extended aromatic ligand (d) capable of complexing two metals.[6] Structurally enforced stacked *polymeric* organometallic materials are fewer in number; two, based on bifacially coordinated 1,3-diborolyl complexes of Ni and Rh, have been reported by Siebert,[7] and a number of stacked group 4 phthalocyanato complexes, prepared by the solid-state condensation of the dihydroxy complexes, have been reported and extensively examined by Marks.[8]

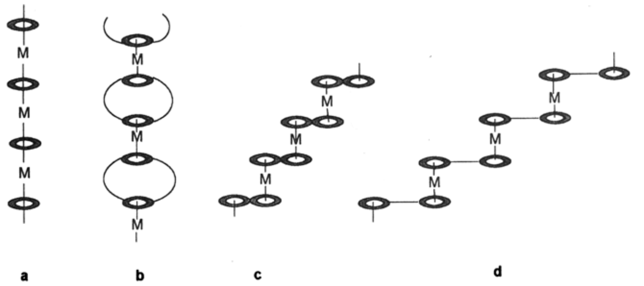

Figure 1.

The present report provides an account of the synthesis and a preliminary study of the properties of metallocene polymers of structural class b, in which contiguous metallocene rings are held in a face-to-face orientation through their peri-substitution on a naphthalene spacer unit.[9]

Experimental Section

General Procedures and Chemicals. Reactions were carried out using standard Schlenk techniques under an argon atmosphere. All solvents were dried before use. THF, ether, petroleum ether, benzene, toluene, and hexane were distilled under nitrogen from sodium; methylene chloride, DMF, and diethylamine were distilled under nitrogen from calcium hydride. Infrared spectra were recorded on a Perkin-Elmer 683 grating infrared spectrometer in a CsI pellet or on a Perkin-Elmer 1650 FTIR in a KBr pellet. ^{1}H NMR data were obtained at 300 MHz and ^{13}C NMR data were obtained at 75 MHz on a Varian XL-300 MHz FTNMR spectrometer. Bulk magnetic susceptibility measurements were obtained on a

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Cahn Div. DTL Faraday magnetic susceptibility balance at room temperature. UV–vis spectra were recorded on a Hewlett Packard 8452A diode array spectrophotometer. High performance liquid chromatography analyses were done using a system incorporating a Waters Model 410 automated gradient controller, two Model 510 pumps, a Model U6-K injector, and a Model 440 UV detector with either a Hewlett Packard Model 3390-Å integrator with a Waters 746 data module or a Waters Model 410 refractive index detector. Waters 100-, 500-, and 10^4-Å Ultrastyragel GPC columns were used in series for polymer analysis, running toluene or unstabilized THF as solvent at 1.0 mL/min. A Waters μ-porasil column was used for general analysis. The calibration curve for polymer analysis was established using polystyrene standards. Elemental analyses were performed by Desert Analytics Inc., Tuscon, AZ. Polymer molecular weight determinations were performed either at Brandeis University using the instrumentation described above or at Loctite Corp., Newington, CT, using a system incorporating Waters Maxima software, a Waters 600E controller, a Waters 410 differential refractometer, and two B&J 9725*DK GPC columns. A calibration curve was established using polystyrene standards. Two probe conductivity studies of oxidized polymer samples were carried out on powder samples packed between two metal rods in a Teflon tube. Contact was made to the two metal rods, and the sample was squeezed in an ordinary vise until the resistance became constant. Four probe dc measurements as a function of temperature were carried out on samples of appropriate geometry utilizing an automatic data acquisition system controlled by a computer interfaced with Keithley measuring devices. Samples were fitted with four probes using small gold wire and conducting paint. The operation was performed under a low-power stereomicroscope. Samples, the heater, and the thermometer were all mounted on a helium cold finger inside a vacuum shroud. Two constant-current sources, capable of reversing the current direction, provided a current of 1–10 μA to the samples and thermometer. A power supply provided current to the heater, and a nanovoltmeter was used to measure the sample voltage, while an ordinary voltmeter measured the thermometer voltage. Samples for Mössbauer studies were mounted in the tail of a flow-type helium-4 cryostat (Supervaritemp Model, Janis Research Co.). Solid or liquid nitrogen was used for the range 298–48 K, and liquid helium was used as the cryogen for the range 48–4.2 K. Temperature control was achieved by using both the calibrated silicon diode/sample-block-heater setup and the nitrogen or helium vapor pressure thermometry/vacuum-regulator setup. The Mössbauer spectra were determined by using a conventional constant-acceleration spectrometer (Canberra Series 35) in conjunction with a Kr/CO_2 gas proportional counter. The γ-ray source was a 70-mCi ^{57}Co in a rhodium metal matrix. Curve fitting of the Mössbauer spectra was accomplished by using a program that incorporates statistical goodness-of-fit and reliability test.[10]

Ferrous chloride was prepared by the method described by Kovacic and Bruce.[11] Ferrous chloride·2THF complex was prepared by the method described by Herzog *et al.*[12] Ferrous acetylacetonate was prepared by the method described by Bunel *et al.*[13] The $NiBr_2$·glyme complex was prepared by the method described by King.[14]

1,8-Diiodonaphthalene (**2**) was prepared by the method of House *et al.*[15] The crude product was recrystallized from hexane and sublimed (100 °C at 0.04 Torr) to yield 20.0 g (49%) of a pale yellow solid. Mp: 107–109 °C (lit. mp[15] 109 °C). ^1H NMR ($CDCl_3$): δ 7.08 (dd, 2H, J = 8.3, 7.4 Hz, ArH_3), 7.85 (dd, 2H, J = 8.3, 1.2 Hz, ArH_4), 8.42 (dd, 2H, J = 7.4, 1.2 Hz, ArH_2). ^{13}C NMR ($CDCl_3$): δ 96.0 (C_1), 126.9 (C_4), 131.0 (C_3), 132.1 (C_{4a}), 135.7 (C_{8a}), 144.0 (C_2).

1-(1′-Cyclopentadienyl and 2′-cyclopentadienyl)-8-iodonaphthalene (**4**). A flame-dried 100-mL Schlenk flask was charged with a copper(I) bromide–dimethyl sulfide complex (819 mg, 3.98 mmol). After purging with argon, the complex was suspended in 10 mL of THF and stirred for 30 min at room temperature. The milky, white suspension was then cooled to −23 °C, and a solution of cyclopentadienyllithium (prepared from a 2.5 M solution of n-butyllithium in hexane (1.6 mL, 3.98 mmol) and freshly cracked cyclopentadiene (0.65 mL, 7.96 mmol) in 10 mL of THF at 0 °C and precooled to −78 °C) was added. The reaction mixture was stirred for 1 h, during which time it turned into a homogeneous yellow solution. A solution of 1,8-diiodonaphthalene (1.10 g, 2.89 mmol) in 6 mL of THF was cooled to −78 °C and added to the $CpCu-S(CH_3)_2$ solution. The reaction was monitored by HPLC (using a μ-porasil analytical column, hexane–CH_2Cl_2 solvent system at a gradient elution flow of 1.5 mL/min) and was quenched in 100 mL of saturated aqueous NH_4Cl, when the starting material peak at V_R = 4.06 had disappeared (*ca.* 2 h). The crude product was extracted into ether, and the combined extracts were dried over $MgSO_4$. This solution was filtered, solvent was removed, and the brown residue was extracted with hexane (5 × 30 mL). The hexane extracts were filtered, concentrated to approximately 20 mL, and flash chromatographed (silica/hexane). The band at R_f = 0.34 was collected to yield 451 mg (49%) of the desired product as a pale yellow oil. ^1H NMR of the major isomer ($CDCl_3$): δ 3.14 (s, 2H, $CpCH_2$), 6.30–6.70 (m, 3H, vinyl H), 7.10 (dd, 1H, J = 7.3, 8.1 Hz, H_6), 7.42 (d, 1H, J = 5.5 Hz, H_4), 7.43 (d, 1H, J = 4.1 Hz, H_2), 7.79 (dd, 1H, J = 5.5, 4.1 Hz, H_3) 7.91 (dd, 1H, J = 8.1, 1.3 Hz, H_5), 8.21 (dd, 1H, J = 7.3, 1.3 Hz, H_7). ^{13}C NMR ($CDCl_3$): δ 48.83 ($CpCH_2$), 92.23 (C_8), 125.07 (C_2), 126.35 (C_6), 128.75 (C_3), 129.59 (C_5), 129.72 (C_4), 132.09 (ipso), 132.40 (ipso), 132.67 (ipso), 133.39 (vinyl), 134.34 (vinyl), 135.3, 141.7 (C_7).

1,1′-Bis(8-iodo-1-naphthyl)ferrocene (7). A Schlenk flask was charged with a solution of 1-cyclopentadienyl-8-iodonaphthalene (413 mg, 1.29 mmol) in 10 mL of THF. The solution was cooled to 0°, and a 1.0 M solution of $NaN(SiMe_3)_2$ in THF (1.29 mL, 1.29 mmol) was added. The solution turned a bright red/orange, was allowed to stir for 30 min, and was then transferred to a 100-mL flame-dried Schlenk flask containing a slurry of $FeCl_2$ (407 mg, 3.22 mmol) in 10 mL of THF, cooled to 0 °C. The reaction mixture, which immediately turned a dark maroon color,was allowed to warm to room temperature and stirred for 2 h. Solvent was removed, the residue was extracted with a solution of 20% (v/v) CH_2Cl_2 in hexane, and the extracts were filtered and flash chromatographed. The first of two bands collected yielded 230 mg (52%) of the desired product **7** as a bright red solid. Mp: 171 °C (dec). ^1H NMR ($CDCl_3$): δ 4.33 (t, 4H, J = 1.8 Hz, 3,4-CpH), 4.47 (t, 4H, J = 1.8 Hz, 2,5-CpH), 7.00 (dd, 2H, J = 8.1, 7.5 Hz, H_6), 7.25 (dd, 2H, J = 8.1, 7.2 Hz, H_3), 7.65 (dd, 2H, J = 8.1, 1.2 Hz, H_4), 7.81 (dd, 2H, J = 8.1, 1.2 Hz, H_5), 8.10 (dd, 2H, J = 7.5, 1.2 Hz, H_7), 8.28 (dd, 2H, J = 7.2, 1.2 Hz, H_2). ^{13}C NMR ($CDCl_3$): δ 69.65 (3,4-CpC), 75.78 (2,5-CpC), 90.87 (ipso CpC), 92.44 (C_8), 123.50 (C_1), 124.66 (C_3), 126.06 (C_6), 127.79 (C_4), 129.28 (C_5), 133.77 (C_2), 135.28 (napthyl), 136.70 (naphthyl), 141.75 (C_7). The second band yielded 140 mg (34%) of the starting material. Anal. Calcd for $C_{30}H_{20}FeI_2$: C, 52.21; H, 2.92. Found: C, 52.17; H, 2.89.

1,1′-Bis(8-cyclopentadienyl-1-naphthyl)ferrocene (8). A Schlenk flask was charged with a copper(I) bromide–dimethyl sulfide complex (776 mg, 3.77 mmol). After purging with argon, the complex was suspended in 10 mL of THF and stirred for 30 min. The milky, white suspension was then cooled to −23 °C, and a solution of cyclopentadienyllithium (prepared from a 2.5 M solution of n-butyllithium in hexane (1.50 mL, 3.77 mmol) and cyclopentadiene (0.621 mL, 7.54 mmol) in 10 mL of THF at 0 °C and precooled to −78 °C) was added. The resulting homogeneous yellow solution was stirred for 1 h. A solution of 1,1′-bis(8-iodo-1-naphthyl)ferrocene (**7**; 100 mg, 0.145 mmol) in 6 mL of THF was cooled to −78 °C and added to this. The reaction was maintained at −23 °C for 20 h, at which time starting material had been consumed. The reaction was quenched in a NH_4Cl solution, and the solution was extracted with ether. The organic phase was dried over $MgSO_4$ and filtered, and the solvent was removed. The residue was extracted with a solution of 20% (v/v) CH_2Cl_2 in hexane (4 × 5 mL), and the extracts were filtered and flash chromatographed on silica to yield 80 mg (97%) of the desired product as a bright red solid. Mp 130 °C (dec). ^1H NMR ($CDCl_3$): δ 2.78–2.85 (m, 4H, $CpCH_2$), 3.81 (t, 4H, J = 1.8 Hz, 3,4-CpH), 4.01 (t, 4H, J = 1.8 Hz, 2,5-CpH), 5.90–6.20 (m, 6H, vinyl), 7.18 (dd, 2H, J = 7.9, 7.1 Hz, H_3), 7.40

(dd, 2H, J = 7.1, 1.5 Hz, H_7), 7.39 (dd, 2H, J = 7.9, 7.1 Hz, H_6), 7.68 (dd, 2H, J = 7.9, 1.5 Hz, H_5), 7.74 (dd, 2H, J = 7.9, 1.5 Hz, H_4), 7.82 (dd, 2H, J = 7.1, 1.5 Hz, H_2).

6-Methyl-6-(1-heptyl)fulvene. This was prepared by the method of Hafner[16] to give 13.80 g (78.4 mmol, 84%) of the desired fulvene as an orange oil. ^1H NMR ($CDCl_3$): δ 0.8–0.95 (m, 3H, CH_3), 1.2–1.6 (m, 8H, CH_2), 2.19 (s, 3H, CH_3), 2.52 (t, 2H, CH_2), 6.45 (m, 4H, vinyl).

2-Octyl-1- and 2-cyclopentadiene. Following the method of Hafner,[16] a 100-mL Schlenk flask was charged with lithium aluminum hydride (1.68 g, 44.0 mmol) and 10 mL of ether. A solution of the fulvene (8.29 g, 47 mmol) in 10 mL of ether was added slowly. The reaction was stirred at room temperature for 2 h, and then 50 mL of cold methanol was added followed by a 2 N HCl solution. The organic solution was dried over $MgSO_4$ and, after removal of solvent, gave 7.87 g (95%) of the product as a pale yellow oil. ^1H NMR ($CDCl_3$): δ 0.8–0.91 (m, 3H, CH_3), 1.10 (dd, 3H, CH_3), 1.15–1.5 (m, 10H, CH_2), 2.46–2.61 (m, 1H, CH), 2.80–2.96 (m, 2H, $CpCH_2$), 5.95–6.0 (m, vinyl), 6.15 (m, vinyl), 6.20–6.29 (m, vinyl), 6.40–6.45 (m, vinyl), 6.49–6.52 (m, vinyl). ^{13}C NMR ($CDCl_3$): δ 13.98, 14.10, 20.18, 21.21, 22.63, 22.69, 27.41, 27.46, 28.28, 29.41, 29.48, 31.66, 31.89, 34.19, 35.11, 36.53, 37.58, 40.20, 40.79, 40.89, 124.35, 125.11, 126.02, 126.51, 130.17, 130.65, 132.18, 132.80, 133.38, 133.47, 152.65, 155.49.

1-(8-Iodo-1-napthyl)-3- and 4-(2-octyl)cyclopentadiene (11a). A 100-mL Schlenk flask was charged with a copper(I) bromide–dimethyl sulfide complex (1.02 g, 5.3 mmol). The complex was suspended in 10 mL of THF and stirred at room temperature for 30 min. The suspension was then cooled to −23 °C, and a solution of 2-octylcyclopentadienyllithium (prepared from a 2.5 M solution of n-butyllithium in hexane (2.13 mL, 5.3 mmol) and 2-octylcyclopentadiene (1.14 g, 6.4 mmol) in 10 mL of THF at 0 °C precooled to −78 °C) was added. The homogeneous yellow solution was stirred for 1 h. A solution of 1,8-diiodonaphthalene (1.40 g, 3.7 mmol) in 6 mL of THF was cooled to −78 °C and added to the cyclopentadienide solution. The reaction was maintained at −23 °C for 8 h and then quenched in aqueous NH_4Cl and extracted with ether. After drying over $MgSO_4$, the ether was removed and the brown oily residue was extracted with hexane. The hexane extracts were filtered, concentrated, and flash chromatographed (silica/hexane) to yield 990 mg (63%) of **11a** isomers, as a yellow oil. ^1H NMR ($CDCl_3$): major isomer, δ 0.9–1.3 (m, 16H, CH_3, CH_2), 2.4–2.6 (m, 1H, CH), 3.0–3.3 (m, 2H, $CpCH_2$), 6.15 (t, 1H, J = 1.3 Hz, CpH_4), 6.36 (d, 1H, J = 0.6 Hz, CpH_2), 7.06–7.13 (m, 1H, ArH_6), 7.42 (d, 1H, J = 5.5 Hz, ArH_4), 7.43 (d, 1H, J = 4.18 Hz, ArH_2), 7.79 (dd,1H, J = 5.5, 4.1 Hz, ArH_3), 7.91 (dd, 1H, J = 8.1, 1.3 Hz, ArH_5), 8.21 (dd, 1H, J = 7.3, 3 Hz, ArH_7); minor isomer, δ 0.9–1.3 (m, 16H, CH_3CH_2), 2.4–2.6 (m, 1H, CH), 3.0–3.3 (m, 2H, $CpCH_2$), 6.26 (m, 1H, CpH_3), 6.30 (m, 1H, CpH_2), 7.06–7.13 (m, 1H, ArH_6), 7.42 (d, 1H, J = 5.5 Hz, ArH_6), 7.43 (d, 1H, J = 4.18 Hz, ArH_2), 7.79 (dd, 1H, J = 5.5, 4.1 Hz, H_3), 7.91 (dd, 1H, J = 8.1, 1.3 Hz, ArH_5), 8.21 (dd, 1H, J = 7.3, 1.3 Hz, ArH_7). ^{13}C NMR ($CDCl_3$): δ 14.14, 22.66, 22.73, 29.50, 31.59, 31.97, 36.56, 37.74, 47.52, 92.23, 125.01, 125.11, 126.26, 126.35, 128.45, 129.47, 129.51, 129.55, 129.63, 130.96, 133.80, 141.57, 141.66. Anal. Calcd for $C_{23}H_{27}I$: C, 64.18; H, 6.27. Found: C, 64.67; H, 6.45.

1,1′-Bis(8-iodo-1-naphthyl)-3,3′-bis(2-octyl)ferrocene (12a). A 50-mL Schlenk flask was charged with a solution of **11a** (700 mg, 1.63 mmol) in 10 mL of THF. The solution was cooled to 0 °C, and a 1.0 M solution of $NaN(SiMe_3)_2$ in THF (2.80 mL, 2.80 mmol) was added dropwise. The solution was stirred for 30 min, during which time it developed a dark red color. At this time, a slurry of anhydrous $FeCl_2$ (400 mg, 3.00 mmol) in 10 mL of THF was added. The reaction mixture was warmed to room temperature and allowed to stir overnight, at which time it showed two major spots at R_f = 0.32 and 0.55 on TLC (silica/10% CH_2Cl_2 in hexane). Solvent was removed, and the residue was extracted with a solution of 10% (v/v) CH_2Cl_2 in hexane. The extracts were flash chromatographed (silica/10% (v/v) CH_2Cl_2 in hexane), and the band which corresponded to the spot at R_f = 0.32 was collected to yield 538 mg (0.58 mmol, 72%) of the desired product as a bright red oil. ^1H NMR ($CDCl_3$): δ 0.9–1.3 (m, 32H, CH_3,CH_2), 2.4–2.6 (m, 2H, CH), 4.0–4.36 (m, 6H, FcH), 6.98–7.13 (m, 4H, ArH_6, ArH_3), 7.59 (dd, 2H, J = 8.1, 1.2 Hz, ArH_4), 7.80 (dd, 2H, J = 8.1, 1.2 Hz, ArH_5), 8.10 (dd, 2H, J = 7.5, 1.2 Hz, ArH_7), 8.08–8.12 (m, 2H, ArH_2). ^{13}C NMR ($CDCl_3$): δ 14.12, 22.65, 22.71, 27.68, 29.46, 29.50, 31.58, 31,96, 38.61, 69.65, 75.13, 78.48, 90.87, 92.50, 124.59, 124.61, 125.94, 127.41, 129.26, 133.72, 133.81, 133.88, 141.61. Anal. Calcd for $C_{46}H_{52}FeI_2$: C, 60.39; H, 5.68. Found: C, 65.29; H, 6.27. The high C and H figures are due to partial loss of iodine (estimated to be 7%) in the conversion of **11a** to **12a**. This monoiodo impurity could not be separated from **12a** on repeated chromatography.

1,1′-Bis(8-cyclopentadienyl-1-naphthyl)-3,3′-bis(2-octyl)ferrocene (13a). A 100-mL Schlenk flask was charged with a copper bromide–dimethyl sulfide complex (2.08 g, 10.1 mmol). The complex was suspended in 10 mL of THF and then cooled to −23 °C. A solution of cyclopentadienyllithium (10.1 mmol, prepared as before and cooled to −78 °C) was added to this. The resulting yellow solution was stirred for 1 h, and a solution of **12a** (335 mg, 0.36 mmol) in 6 mL of THF, cooled to −78 °C, was added to it. The reaction was maintained at −23 °C for 24 h, at which time TLC (silica/10% (v/v) CH_2Cl_2 in hexane) of the reaction verified the disappearance of the starting material at R_f = 0.32 and the appearance of a new spot at R_f = 0.30 (also red in color). The reaction was worked up as before. The dried extracts were filtered, concentrated, and flash chromatographed (silica/10% (v/v) CH_2Cl_2 in hexane). The band which corresponded to the spot at R_f = 0.30 was collected to yield 283 mg (0.35 mmol, 98%) of **13a** as a bright red oil. ^1H NMR ($CDCl_3$): δ 0.8–1.3 (m, 32H, CH_3,CH_2), 2.2–2.4 (m, 2H, CH), 2.6–2.7 (m, 1H, $CpCH_2$), 2.75–2.88 (m, 1H, $CpCH_2$), 3.5–4.0 (m, 6H, FcH), 5.8–6.3 (m, 6H, vinyl CpH), 6.9–7.05 (m, 4H, ArH_3, ArH_7), 7.29 (dd, 2H, J = 7.1, 1.5 Hz, ArH_6), 7.33–7.41 (m, 2H, ArH_5), 7.58–7.68 (m, 2H, ArH_4), 7.74 (dd, 2H, J = 7.1, 1.5 Hz, ArH_2). ^{13}C NMR ($CDCl_3$): δ 14.17, 22.74, 22.76, 27.80, 29.48, 31.90, 31.99, 32.52, 41.31, 69.65, 75.78, 78.50, 123.70, 123.73, 124.14, 124.70, 126.30, 127.35, 128.16, 128.18, 128.37, 130.27, 131.50, 131.54, 131.57, 131.60, 131.99, 132.45.

Polymerization of 13a. Preparation of Ferrocene Polymer 14b. A flame-dried 50-mL Schlenk flask was charged with a solution of **13a** (205 mg, 0.26 mmol) in 10 mL of THF. The solution was cooled to 0 °C, and a 0.88 M solution of $NaN(SiMe_3)_2$ in THF (0.63 mL, 0.56 mmol) was added dropwise. The solution was stirred for 30 min, and a slurry of $FeCl_2$ (33 mg, 0.26 mmol) in 10 mL of THF was added. The reaction was warmed to room temperature and allowed to stir overnight. The reaction was monitored by HPLC over a period of 10 days, during which time successive amounts of base and $FeCl_2$ were added (10% of calculated molar amounts of both, four times), until there was no longer any change in gel permeation retention volumes. Solvent was then removed, and the residue was extracted with toluene and filtered. After removal of toluene, the product was washed with ether and methanol to remove low molecular weight and inorganic materials, leaving 215 mg of product (71%) as a dark purple solid. M_n = 14,363; M_w = 18 398, PDI = 1.28, and V_R = 19.93 mL. End-group proton analysis M_n: vinylCp/aryl, 18 000; vinylCp/(ferrocenyl + aliphatic), 17 700. IR (KBr): 3036, 2942, 2907, 2848, 1572, 1501, 1460, 1366, 1055, 1031, 820, 767 cm^{-1}. IR (CsI): 430 cm^{-1}. ^1H NMR ($CDCl_3$): δ 0.8–1.4 (CH_3,CH_2), 3.5–4.0 (FcH), 5.8–6.2 (CpH), 6.8–7.8 (ArH). Anal. Calcd for $[C_{56}H_{61}Fe_2(C_{56}H_{60}Fe_2)_nC_{56}H_{61}Fe]$ (n = 30–100): Fe, 13.08–13.21; I, 0.00. Found: Fe, 13.67; I, 0.00.

When this reaction was carried out in refluxing THF for 4 days, 160 mg of polymer **14a**, largely insoluble in THF, was isolated.

Resubmission of a Polymer after Isolation. A 100-mL flame-dried Schlenk flask was charged with 275 mg (*ca.* 0.27 mmol, estimated mol wt 1000) of a low molecular weight polymer sample isolated from a previous reaction, which gave a broad GPC trace with retention volume maxima at V_R = 22, 23, and 25 mL. This polymer was dissolved in 10 mL of THF, the solution was cooled to 0 °C, and a 1.0 M solution of $NaN(SiMe_3)_2$ in THF (0.82 mL, 0.82 mmol) was added. The solution was stirred for 20 min, at which time a THF slurry of $FeCl_2$ (35 mg, 0.27 mmol) was added. The reaction was slowly heated to reflux and was stirred overnight. At that time, the solution, analyzed by HPLC, showed a GPC curve that had shifted toward higher molecular weight components (V_R = 21 mL) at the expense of lower molecular weight components (V_R = 23 and 25 mL). Solvent was removed, and the residue was extracted with ether and then benzene. The ether extracts yielded 122 mg (40%) of low molecular weight polymer with M_n = 3360 and M_w = 6730 (V_R = 21.7). The benzene extracts yielded 148 mg (49%) of higher molecular weight polymer with M_n = 5200 and M_w = 1 2 800, with a peak max = 15 120 and V_R= 20 mL.

Preparation of Ferrocene–Nickelocene Copolymer (14f). Following the above procedure for the preparation of polymer **14a**, a THF solution of $Ni(acac)_2$ (132 mg, 0.51 mmol) was added to the dianion, generated from **8** (125 mg, 0.22 mmol) at −78 °C by treatment with 0.55 mL (0.55 mmol) of a 1.0 M solution of $NaN(SiMe_3)_2$ in THF. The polymerization was carried out at room temperature and was stopped after 1 day. The product was washed successively with ether, toluene, and methanol, leaving 66 mg of **14f** (54%) as a dark purple solid, which was slightly soluble in THF. The THF-soluble material gave M_n = 1785, M_w = 2968, PDI = 1.66 (bimodal peak distribution with a small peak at 30 449) and V_R = 21.0 mL. End-group proton analysis M_n: aryl/vinylCp, 2526; aryl/$CpCH_2$, 2638; ferrocenyl/vinylCp, 2205; ferrocenyl/$CpCH_2$, 2283. ^1H NMR ($CDCl_3$) of the toluene-soluble fraction: δ −270 to −255 (Cp_2Ni), 2.4−2.8 ($CpCH_2$), 3.5−4.4 (FcH), 5.8−6.2 (vinyl CpH), 6.9−7.8 (ArH). Anal. Calcd for $[C_{40}H_{29}Fe(C_{40}H_{28}FeNi)_nC_{40}H_{29}FeNi]$ n = 2−4): Fe, 9.19−9.13; Ni, 7.26−8.01. Found: Fe; 9.23; Ni, 7.40.

Polymerization of 13a. Preparation of Ferrocene–Nickelocene Copolymer (14g). Following the above procedure for the preparation of polymer **14b**, a THF solution of $Ni(acac)_2$ (44 mg, 0.17 mmol) was added to the dianion, generated at 0 °C from **13a** (135 mg, 0.17 mmol) by treatment with 0.34 mL (0.34 mmol) of a 1.0 M solution of $NaN(SiMe_3)_2$ in THF. The polymerization was stopped after 4 days (with two successive additions of 20 mol % of both $Ni(acac)_2$ and base during this period). Solvent was removed from the reaction, and the product was washed successively with ether, toluene, and methanol to yield 110 mg of polymer **14g** (54%) as a dark purple solid, which was insoluble in THF. IR (KBr): 3036, 2942, 2907, 2848, 1584, 1519, 1454, 1366, 1037, 820, 767 cm^{-1}. IR (CsI): 440, 390 cm^{-1}. μ_{eff} = 3.51 μ_B. Anal. Calcd for $[C_{56}H_{61}Fe(C_{56}H_{60}FeNi)_nC_{56}H_{61}FeNi]$ (n = 10−100): Fe, 6.65−6.62; Ni, 6.65−6.90; I, 0.00. Found: Fe, 6.63; Ni, 6.94; I, 0.16. Ni/Fe. Calcd for n = 10−100: 0.96−1.04. Found: 1.04.

Polymerization of 13a. Preparation of Ferrocene–Cobaltocene Copolymer (14i). Following the above procedure for the preparation of polymer **14b**, a THF solution of $CoCl_2$ (15.0 mg, 0.114 mmol) was added to the dianion generated at 0 °C from **13a** (90.0 mg, 0.114 mmol) by treatment with 0.28 mL (0.28 mmol) of a 1.0 M solution of $NaN(SiMe_3)_2$ in THF. The polymerization was allowed to proceed at room temperature and was quenched after 3 days. Solvent was removed and the solid residue was extracted with THF and filtered. The THF-insoluble fraction was isolated to yield 84 mg (88%) of polymer **14i** as a black solid (higher molecular weight polymer). IR (CsI): 828, 770, 450, 380 cm^{-1}. μ_{eff} = 5.2 μ_B. The THF-soluble fraction was purified further by removal of solvent and washing the solid successively with ether and H_2O to remove low molecular weight components and $CoCl_2$. This yielded 10 mg (10%) of oligomeric material as a black solid. ^1H NMR ($CDCl_3$): δ −56 to −78 (Cp_2Co), 0.8−1.8 (CH_2, CH_3), 2.0−2.4 ($CpCH_2$), 3.2−4.0 (Fc), 4.8−5.8 (vinyl CpH), 6.9−8.0 (ArH). End-group analysis M_n: vinyl Cp/aliphatic, 1637; vinyl Cp/aryl, 1227; vinyl Cp/ferrocene, 1023.

1,1′-Bis[8-(3- and 4-(2-octyl)cyclopentadienyl)-1-naphthyl]-3,3′- and 3,4′-bis(2-octyl)ferrocene (13c). Following the above procedure for the preparation of **13a**, a solution of 2-octylcyclopentadienyllithium was prepared from 2-octylcyclopentadiene (1.38 g, 7.7 mmol) and a 2.5 M solution of *n*-butyllithium in hexane (2.69 mL, 6.74 mmol) in 10 mL of THF at 0 °C. The solution was precooled to −78 °C and was added to a suspension of $CuBr-SMe_2$ (1.37 g, 6.74 mmol) in THF. After the addition of **12a** (200mg, 0.22 mmol) and workup, 205 mg of **13c** was isolated (93%) as a bright red oil. ^1H NMR ($CDCl_3$): δ 0.6−1.5 (m, 64H, CH_3,CH_2), 2.1−2.4 (m, 4H, CH), 2.7−2.95 (m, 4H, $CpCH_2$), 3.5−4.5 (m, 6H, FcH), 5.58−6.18 (m, 4H, CpH), 7.2−7.8 (m, 12H, ArH). ^{13}C NMR ($CDCl_3$): δ 14.12, 14.17, 22.70, 22.75, 27.21, 27.37, 27.50, 27.67, 27.76, 27.85, 27.87, 29.18, 29.47, 29.70, 31.84, 31.87, 31.93, 31.96, 43.52, 43.55, 68.14, 70.82, 123.96, 124.67, 124.71, 125.08, 125.16, 125.21, 125.26, 125.41, 125.44, 125.47, 125.50, 125.86, 125.89, 125.97, 126.00, 126.08, 126.18, 126.22, 127.86, 128.86, 128.79, 130.86, 131.29, 133.81.

Polymerization of 13c. Preparation of Ferrocene Polymer 14c. Following the above procedure for the preparation of polymer **14b**, a THF slurry of $FeCl_2$ (30 mg, 0.24 mmol) was added to the dianion, generated from **13c**, at 0 °C (205 mg, 0.20 mmol) by treatment with 0.50 mL of a 1.0 M solution of $NaN(SiMe_3)_2$ (0.50 mmol) in THF. The reaction mixture was heated under reflux for 10 days, during which time 20 mol % of $FeCl_2$ and base was added three times. Solvent was then removed, and the product was washed successively with hexane, ether, warm toluene, and methanol, leaving 167 mg of polymer **14c** (50%) as a dark purple solid, which was only slightly soluble in THF. M_n = 934, M_w = 5169 (bimodal peak distribution with a small peak at 136 000 and much larger peak at 2900). IR (KBr): 3042, 2950, 2925, 2858, 1649, 1565, 1457, 1340, 1048, 823, 768 cm^{-1}. IR (CsI) 430 cm^{-1}. Anal. Calcd for $[C_{72}H_{93}Fe_2(C_{72}H_{92}Fe_2)_nC_{72}H_{93}Fe]$ (n = 10−100): Fe, 10.09−10.44; I, 0.00. Found: Fe, 10.09; I, 0.00.

Preparation of Ferrocene–Nickelocene Copolymer 14h. Following the above procedure for the preparation of polymer **14g**, a solution of $NiBr_2$·glyme (88.0 mg, 0.22 mmol) in 5 mL of THF was added to the dianion, generated from **13c**, at 0 °C (196.0 mg, 0.19 mmol) and 0.60 mL of a 0.70 M solution of $NaN(SiMe_3)_2$ (0.42 mmol) in THF. Polymerization was allowed to proceed at room temperature for 4 days and at reflux temperature for 24 h, during which time two successive additions of 20 mol % of $NiBr_2$·glyme and base was carried out. Solvent was then removed, and the product was washed successively with hexane, ether, benzene, and methanol to yield polymer **14h** as a dark purple solid, which was only partially soluble in THF. M_n = 1511, M_w = 5681. Benzene-soluble fraction: M_n = 1239, M_w = 4427.

Reduction of Citral. Citral (5.8 mL, 32.0 mmol) was taken up in 80 mL of ethanol and reduced in a 250-mL Parr Shaker flask in the presence of 10% Pd on carbon (500 mg) to give 5.0 g (97%) of the desired tetrahydrocitral[17] as a colorless liquid. ^1H NMR ($CDCl_3$): δ 0.9 (d, 6H, CH_3), 1.01 (d, 3H, CH_3), 1.1−1.4 (m, 6H, CH_2), 1.49−1.60 (m, 1H, CH), 2.0−2.1 (m, 1H, CH), 2.18−2.45 (m, 2H, CH_2), 9.75 (m, 1H, HCO). ^{13}C NMR ($CDCl_3$): δ 20.36, 22.93, 23.02, 25.05, 28.29, 28.57, 37.52, 39.38, 51.48, 203.50.

6-(2,6-Dimethylheptyl)fulvene. Following the method of Little,[18] a solution of diethylamine (2.3 mL, 22.0 mmol) in methanol was added to a solution of 3,7-dimethyloctanal (4.5 g, 28.8 mmol), prepared above, and freshly cracked cyclopentadiene (5.6 mL, 68.0 mmol) and 30 mL of methanol, at 0 °C. After the addition of glacial acetic acid (3.25 mL, 56.7 mmol) to the bright yellow solution and workup, 5.70 g (97%) of the fulvene was isolated as an orange liquid. ^1H NMR ($CDCl_3$): δ 0.85 (d, 6H, CH_3), 0.95 (d, 3H, CH_3), 1.1−1.4 (m, 6H, CH_2), 1.45−1.6 (m, 1H, CH), 1.6−1.75 (m, 1H, CH), 2.3−2.6 (m, 2H, CH_2), 6.2 (m, 1H, vinyl), 6.4−6.55 (m, 4H, fulvene). ^{13}C NMR ($CDCl_3$): δ 20.22, 23.00, 23.09, 25.25, 28.37, 34.01, 37.50, 38.70, 39.57, 119.73, 125.94, 131.00, 133.32, 142.65, 147.16.

1-(3,7-Dimethyloctyl)- and 2-(3,7-dimethyloctyl)cyclopentadiene. Following the above procedure for the preparation of 2-octylcyclopentadiene, an ether solution of the above fulvene (5.57 g, 27.3 mmol) was added to a suspension of lithium aluminum hydride (918 mg, 24.1 mmol) in ether. After similar workup, 5.60 g (99%) of the desired cyclopentadiene was isolated as a yellow liquid (mixture of double bond isomers). ^1H NMR ($CDCl_3$): δ 0.8−0.95 (m, 9H, CH_3), 1.1−1.6 (m, 10H, CH_2, CH), 2.3−2.45 (m, 2H, CH_2), 2.85−2.98 (m, 2H, $CpCH_2$), 6.0−6.48 (m, 3H, vinyl Cp). ^{13}C NMR ($CDCl_3$): δ 20.01, 23.04, 23.13, 23.23, 25.16, 27.83, 28.40, 28.68, 32.98, 33.02, 36.51, 37.42, 37.61, 39.77, 41.60, 43.69, 125.87, 126.36, 130.71, 132.86, 133.96, 135.27.

1-(8-Iodo-1-napthyl)-3- and 4-(3,7-dimethyloctyl)cyclopentadiene (11b). Following the procedure for the preparation of **11a**, a solution of (3,7-dimethyloctyl)cyclopentadienyllithium was prepared from the cyclopentadiene prepared above (1.34 g, 6.50 mmol) and a 2.5 M solution of *n*-butyllithium in hexane (2.15 mL, 5.39 mmol) in 10 mL of THF at 0 °C. This was precooled to −78 °C and added to a suspension of CuBr-SMe_2 (1.11 g, 5.39 mmol) in THF. After the addition of diiodonaphthalene (1.30 g, 3.42 mmol) and similar workup, 713 mg (46%) of the desired product was isolated as a yellow oil. ^{1}H NMR: major isomer, δ 0.7−0.98 (m, 9H, CH_3), 1.10−1.35 (m, 10H, CH_2, CH), 2.37−2.55 (m, 2H, CH_2), 3.0−3.1 (m, 2H, $CpCH_2$), 6.17 (t, 1H, J = 1.3 Hz, vinyl H_4), 6.32 (d, 1H, J = 0.6 Hz, vinyl H_2), 7.01−7.10 (m, 1H, ArH_6), 7.42 (d, 1H, J = 5.5 Hz, ArH_4), 7.43 (d, 1H, J = 4.18 Hz, ArH_2), 7.71−7.80 (m, 1H, ArH_3), 7.80−7.88 (m, 1H, ArH_5), 8.21 (dd, 1H, J = 7.3, 1.3 Hz, ArH_7); minor isomer, δ 0.7−0.98 (m, 9H, CH_3), 1.10−1.35 (m, 10H, CH_2, CH), 2.37−2.55 (m, 2H, CH_2), 3.0−3.1 (m, 2H, $CpCH_2$), 6.26 (m, 1H, vinyl H_3), 6.30 (m, 1H, vinyl H_2), 7.01−7.10 (m, 1H, ArH_6), 7.42 (d, 1H, J = 5.5 Hz, ArH_4), 7.43 (d, 1H, J = 4.18 Hz, ArH_2), 7.71−7.80 (m, 1H, ArH_3), 7.80−7.88 (m, 1H, ArH_5), 8.21 (dd, 1H, J = 7.3, 1.3 Hz, ArH_7). Anal. Calcd for $C_{25}H_{31}I$: C, 65.64; H, 6.78. Found: C, 65.54; H, 6.58.

1,1′-Bis(8-iodo-1-napthyl)-3,3′-bis(3,7-dimethyloctyl)ferrocene (12b). Following the above procedure for the preparation of **12a**, a 1.0 M solution of $NaN(SiMe_3)_2$ in THF (1.40 mL, 1.40 mmol) was added to a solution of **11b** (500 mg, 1.09 mmol) in THF at 0 °C. After the addition of $FeCl_2$ (200 mg, 1.58 mmol), similar workup, and flash chromatography (silica/5% (v/v) CH_2Cl_2 in hexane), 260 mg of the desired product (50%) was isolated as a bright red oil. ^{1}H NMR ($CDCl_3$): δ 0.8−1.0 (m, 18H, CH_3), 1.0−1.6 (m, 20H, CH_2, CH), 2.30−2.50 (m, 4H, CH_2), 4.0−4.38 (m, 6H, FcH), 7.0−7.13 (m, 4H, ArH_6, ArH_3), 7.59 (dd, 2H, J = 8.1, 1.2 Hz, ArH_4), 7.80 (dd, 2H, J = 8.1, 1.2 Hz, ArH_5), 8.10 (dd, 2H, J = 7.5, 1.2 Hz, ArH_7), 8.15−8.22 (m, 2H, ArH_2). ^{13}C NMR ($CDCl_3$): δ 19.62, 22.64, 22.75, 24.86, 26.80, 27.96, 32.57, 37.30, 38.94, 39.37, 69.65, 75.13, 78.48, 90.87, 92.50, 124.59, 124.61, 125.94, 127.41, 129.26, 133.72, 133.81, 133.88, 141.61.

1,1′-Bis(8-cyclopentadienyl-1-naphthyl)-3,3′-bis(3,7-dimethyloctyl)ferrocene (13b). Following the above procedure for the preparation of **13a**, a solution of cyclopentadienyllithium, prepared at 0 °C from freshly cracked cyclopentadiene (0.43 mL, 5.21 mmol) and a 2.5 M solution of *n*-butyllithium (1.04 mL, 2.60 mmol) in 10 mL of THF, was cooled to −78 °C. This was added to a suspension of CuBr−SMe_2 (538 mg, 2.60 mmol) in THF. After the addition of **12b** (235 mg, 2.42 mmol) and flash chromatography (silica/5% (v/v) CH_2Cl_2 in hexane), 180 mg (88%) of the desired product was isolated as a bright red oil. ^{1}H NMR ($CDCl_3$): δ 0.78−0.9 (m, 18H, CH_3), 1.0−1.4 (m, 20H, CH_2, CH), 2.0−2.2 (m, 4H, CH_2), 2.6−2.85 (m, 4H, $CpCH_2$), 3.5−3.92 (m, 6H, FcH), 5.85−6.22 (m, 6H, vinyl), 6.9−7.09 (m, 4H, ArH_3, ArH_7), 7.25−7.32 (m, 4H, ArH_6), 7.33−7.41 (m, 2H, ArH_5), 7.55−7.69 (m, 2H, ArH_4), 7.74 (dd, 2H, J = 7.1, 1.5 Hz, ArH_2). ^{13}C NMR ($CDCl_3$): δ 19.54, 19.62, 22.65, 22.76, 24.74, 26.30, 26.44, 28.00, 32.73, 37.09, 38.18, 39.41, 44.29, 124.20, 124.24, 124.65, 126.45, 127.46, 128.03, 128.37, 128.47, 130.51, 130.57, 131.74, 131.84, 132.34.

Nonylfulvene. This was prepared from decylaldehyde (12.45 g, 80 mmol) and freshly cracked cyclopentadiene (13.22 g, 200 mmol) in 150 mL of methanol, following the procedure given earlier for the preparation of 6-(2,6-dimethylheptyl)fulvene, and was obtained in 98% yield, as a deep yellow oil. ^{1}H NMR ($CDCl_3$) δ 0.88 (t, 3H, CH_3), 1.15−1.42 (m, 12H, CH_2), 1.43−1.59 (m, 2H, CH_2), 2.48−2.56 (m, 2H, CH_2), 6.18−6.22 (m, 1H, H_6), 6.42−6.55 (m, 4H, vinyl). ^{13}C NMR ($CDCl_3$): δ 14 (CH_3), 22.67, 29.29, 29.35, 29.44, 29.48, 31.08, 31.87 (CH_2), 119.15, 125.60, 130.64, 132.88, 143.47 (vinyl CH).

Decylcyclopentadiene. This was prepared in 98% yield, from decylaldehyde (12.45 g., 80 mmol) and freshly cracked cyclopentadiene (13.22 g., 200 mmol), following the procedure used to prepare 2-octylcyclopentadiene, and was obtained as a yellow oil. An NMR spectrum shows that the product is a mixture of 1- and 2-*n*-decylcyclopentadiene. ^{1}H NMR ($CDCl_3$): δ 0.88 (t, 3H, CH_3), 1.15−1.40 (m, 14H, CH_2), 1.45−1.60 (m, 2H, CH_2), 2.30−2.42 (m, 2H, CH_2), 2.86−2.92 (m, 2H, $CpCH_2$), 5.98−6.46 (m, 3H, vinyl). ^{13}C NMR ($CDCl_3$): δ 14.11 (CH_3), 22.69, 28.89, 29.35, 29.49, 29.53, 29.64, 29.79, 29.88, 30.75, 31.92 (CH_2), 41.19, 43.24 (Cp, CH_2), 125.63, 126.07, 130.32, 132.44, 133.53, 134.84 (vinyl CH).

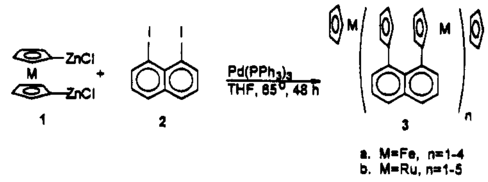
1-(8-Iodo-1-naphthyl)-3- and 4-decylcyclopentadiene (11d) (Major and Minor Isomers). Following the procedure for the preparation of **11a**, a solution of *n*-decylcyclopentadienyllithium was prepared from *n*-decylcyclopentadiene (1.31 g, 6.36 mmol) and a 2.5 M solution of *n*-butyllithium in hexane (1.87 mL, 4.67 mmol) in 10 mL of THF, at 0 °C. The solution was cooled to −78 °C and was added to a suspension of $CuBrSMe_2$ (964 mg, 4.67 mmol) in THF. After the addition of diiodonaphthalene (1.25 g, 3.28 mmol) and similar workup, 665 mg of the desired product (44%) was isolated as a yellow oil. ^{1}H NMR ($CDCl_3$) 1-aryl-3-(1-decylcyclopentadiene), major isomer, δ 0.75−0.90 (m, 3H, CH_3), 1.0−1.5 (m, 16H, CH_2), 2.38−2.55 (m, 2H, CH_2), 3.0−3.15 (m, 2H, $CpCH_2$), 6.17 (t, 1H, J = 1.3 Hz, CpH_4), 6.32 (d, 1H, J = 0.6 Hz, CpH_2), 7.01−7.10 (m, 1H, ArH_6), 7.40−7.44 (d, 1H, J = 5.5 Hz, ArH_4), 7.43 (d, 1H, J = 4.18 Hz, ArH_2), 7.71−7.80 (m, 1H, ArH_3), 7.80−7.88 (m, 1H, ArH_5), 8.21 (dd, 1H, J = 7.3, 1.3 Hz, ArH_7); 1-aryl-4-(1-decylcyclopentadiene), minor isomer, δ 0.75−0.90 (m, 3H, CH_3), 1.0−1.5 (m, 16H, CH_2), 2.38−2.55 (m, 2H, CH_2), 3.0−3.15 (m, 2H, $CpCH_2$), 6.26 (m, 1H, CpH_3), 6.30 (m, 1H, CpH_2), 7.01−7.10 (m, 1H, ArH_6), 7.42 (d, 1H, J = 5.5 Hz, ArH_4), 7.43 (d, 1H, J = 4.18 Hz, ArH_2), 7.71−7.80 (m, 1H, ArH_3), 7.80−7.88 (m, 1H, ArH_5), 8.20 (dd, 1H, J = 7.3, 1.3 Hz, ArH_7).

1,1′-Didecyl-3,3′-Bis(8-iodo-1-naphthyl)ferrocene (12d). The procedure for the preparation of **12a** was used. The crude product was purified by chromatography (silica gel, hexane, then (v/v) 50% ether/hexane) to give 399 mg (72%) of the desired product (mixture of diastereomers) as a red oil. ^{1}H NMR ($CDCl_3$): δ 0.88 (t, 6H, CH_3), 0.90−1.5 (m, 32H, CH_2), 2.25−2.50 (m, 4H, CH_2), 4.00−4.35 (m, 6H, FcH), 6.98−7.05 (m, 1H, ArH_3), 7.04−7.12 (m, 1H, ArH_6), 7.59 (dd, 1H, J = 8.1, 1.2 Hz, ArH_5), 7.81 (dd, 1H, J = 8.1, 1.2 Hz, ArH_2), 8.10 (dd, 1H, J = 7.5, 1.2 Hz, ArH_4), 8.16−8.19 (m, 1H, ArH_7). ^{13}C NMR ($CDCl_3$) (assignments were made with the results of HETCOR experiments): δ 14.1 (CH_3), 22.7, 29.44, 29.55, 29.60, 29.66, 29.61, 31.55, 31.69, 31.92 (CH_2), 69.75, 70.44, 75.26, 75.47, 76.58, 77.00, 77.43, 78.48 (Cp), 89.39, 89.80 (*ipso*-Cp), 92.6 (ArC_8), 124.6 (ArC_3), 125.9 (ArC_6), 127.4 (ArC_4), 129.2 (ArC_5), 133.8 (ArC_1), 133.9 (ArC_2), 135.3, 137.1 (ArC_{4a}, ArC_{8a}), 141.7 (ArC_7).

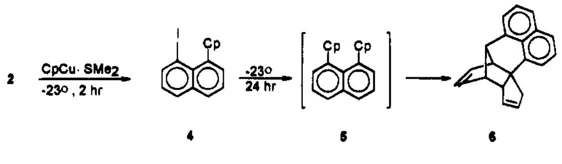
1,1′-Didecyl-3,3′-(8-cyclopentadienyl-1-naphthyl)ferrocene (13d). Following the procedure used in the preparation of **13a**, a solution of cyclopentadienyllithium, prepared from cyclopentadiene (0.23 mL, 2.8 mmol) and *n*-butyllithium (0.63 mL, 1.57 mmol) in 10 mL of THF, was cooled to −78 °C. This was added to a suspension of $CuBrSMe_2$ (323 mg, 1.57 mmol) in 10 mL of THF, cooled to −23 °C. The resulting solution was stirred for 1 h, and then a solution of **12d** (276 mg, 0.28 mmol), cooled to −40 °C was added to the CpCu solution. The mixture was stirred for 20 h at −23 °C and then worked up. Chromatography on silica (hexane) gave 230 mg (94%) of product **13d** as a red oil. ^{1}H NMR ($CDCl_3$) δ 0.89 (t, 6H, CH_3), 1.0−1.6 (m, 32H, CH_2), 2.0−2.15 (m, 4H, CH_2), 2.6−2.8 (2m, 4H, $CpCH_2$), 3.45−3.9 (m, 6H, FcH), 5.8−6.2 (m, 6H, vinyl), 6.9−7.1 (m, 2H, ArH_3), 7.3−7.4 (m, 4H, $ArH_{6,7}$), 7.6−7.8 (m, 6H, $ArH_{2,4,5}$). Anal. Calcd for $C_{60}H_{70}Fe$: C, 85.08; H, 8.33. Found: C, 84.20; H, 8.14.

Nickelocene Polymer 18. A solution of cyclopentadienyllithium was prepared at 0 °C from freshly cracked cyclopentadiene (0.052 mL, 0.63 mmol) in 10 mL of THF and a 2.5 M solution of *n*-butyllithium in hexane (0.24 mL, 0.60 mmol). The solution was cooled to −78 °C and added to a suspension of a copper(I) bromide−dimethyl sulfide complex (125 mg, 0.60 mmol), cooled to −23 °C in a 100-mL Schlenk flask. After 1 h, a solution of **11d** (253 mg, 0.55 mmol) in 5 mL of THF, cooled to −78 °C, was added to this. The resulting solution was stirred at −23 °C for 48 h. A 1.0 M solution of $NaN(SiMe_3)_2$ in THF (1.25 mL, 1.25 mmol) was added to the reaction mixture at −23 °C, and stirred for 30 min. $Ni(acac)_2$ (200 mg, 0.78 mmol) in 5 mL of THF was added, and the mixture was warmed to room temperature. The reaction was periodically monitored by HPLC and was continued for 6 days, during

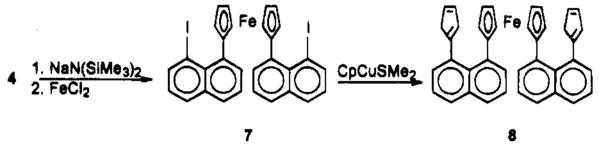
Scheme 1



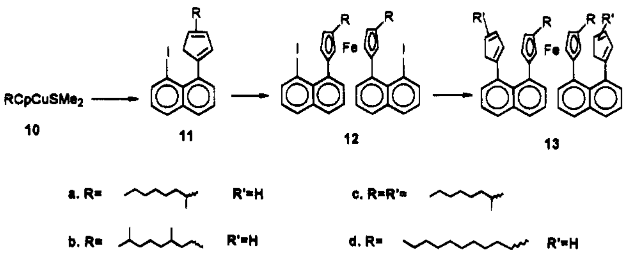
Scheme 2



Scheme 3



Scheme 4



which time two successive additions of Ni(acac)$_2$ and base (20 mol %) were carried out. At the end of this period no change in gel permeation retention volumes of the components was observed. The reaction was poured onto a saturated aqueous NH_4Cl solution and extracted with benzene. The organic layer was recovered and dried over $MgSO_4$. The solvent was removed, and the residue was washed successively with hexane, ether, and methanol to remove lower molecular weight components and Ni(acac)$_2$, respectively, to yield 20 mg (7%) of polymer **18** as a shiny black solid. M_n = 3691, M_w = 6580. IR (KBr): 3048, 2954, 2919, 2848, 1707, 1578, 1513, 1443, 1396, 1260, 1172, 1096, 1020, 796 cm^{-1}. IR (CsI): 360 cm^{-1}. $\mu_{eff} = 5.3\ \mu_B$.

Oxidation of Ferrocene Polymer 14a,b with I$_2$ (General Procedure). A weighed amount of polymer was taken up by 10 mL of CH_2Cl_2 in a 50-mL Schlenk flask under argon, and a volume of a standardized 0.17 M solution of I_2 in benzene, needed to achieve the desired oxidation level calculated on the basis of the stoiciometry of eq 1, was added dropwise. The solution was stirred for 2 h at room temperature, during which time a precipitate formed. Solvent was removed, and the remaining solid was washed several times with ether to yield oxidized polymer as a dark brown or black solid.

Results and Discussion

Several years ago we reported the preparation of 1,8-diferrocenyl- and 1,8-diruthenocenylnaphthalene **3**[19] (n = 1; Scheme 1) and of oligomers[20] derived from them. Although low molecular weight polymers could be isolated from these reactions, the methodology is not well suited to the preparation of high molecular weight polymers of this class, since the high chemical reactivity of the zincated metallocene **1** forecloses its purification. Consequently, it is difficult to achieve the exact stoichiometry of reactants required for maximal polymer yield in such a polycondensation reaction.[21] Moreover, the application of this methodology to a broad range of polymeric congeners based on other metallocenes is problematic, since the metallation of these has not been described.

We sought, therefore, to develop a more general method for the synthesis of these polymers based on bis(cyclopentadienyl)naphthalene **5** (Scheme 2). Cyclopentadienylation of iodobenzenes using cyclopentadienylcopper triethylphosphine[22] had been reported earlier,[23] and we found that reaction of this reagent with **2** gave 1-cyclopentadienyl-8-iodonaphthalene (**4**) in modest yield. However, this copper complex is difficult to prepare, while the more reactive cyclopentadienylcopper–dimethyl sulfide complex is readily available from the reaction of cyclopentadienyllithium and copper bromide–dimethyl sulfide. Reaction of this complex at −23 °C with **2** for 24 h led to the replacement of both iodo substituents and the formation of Diels–Alder product **6**.[24] However, the difference in rates associated with the first and second cyclopentadienylation steps is sufficiently great to allow the isolation of intermediate product **4** in 49% yield, as a mixture of 1-(1- and 2-cyclopentadienyl)-8-iodonaphthalene, when the coupling reaction is quenched at the end of 2 h.

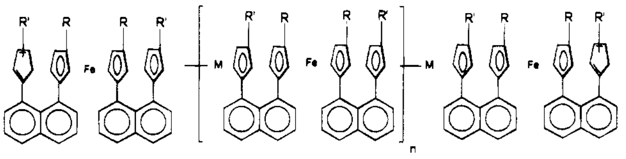
The isolation of **4** provided a potential new route for the preparation of metallocene polymers structurally related to **3**. Thus, treatment of **4** with sodium hexamethyldisilylamide, followed by anhydrous ferrous chloride, gave the ferrocene **7** (52%), which was transformed to the desired monomer **8** (97%) by treatment with excess CpCuSMe$_2$[25] (Scheme 3).

Since polymetallocenes based on structure **3** represent a relatively rigid polymer,[26] the sequence above was first modified so as to improve the solubility of the polymer through introduction of an aliphatic substituent within **8**. Such a general strategy has been applied to improve the solublility of poly(p-phenylene),[27] poly(thiophenes)[28], poly(p-arylenevinylene),[29] poly(p-phenyleneethynylene),[30] and polypyrrole.[31] Substitution of the cyclopentadiene ring is readily achieved by condensation of a cyclopentadienide anion with an aldehyde or ketone and reduction of the resulting fulvene with lithium aluminum hydride. Thus, condensation of cyclopentadienylsodium with 2-octanone, following the method of Hafner,[32] gave the corresponding fulvene **9**, which was reduced with lithium aluminum hydride and quenched to give **10a** (95%; Scheme 4). This was converted to the copper salt through successive treatment with n-butyllithium and copper bromide–dimethyl sulfide and coupled with **2** to give **11a** in 72% overall yield. Small amounts of perylene and 1-iodonaphthalene were isolated from these reactions, but the Diels–Alder reaction product corresponding to **6** was not observed, even on prolonged reaction in the presence of an excess of the cyclopentadienylcopper salt.

The PMR spectrum of **11a** shows it to be a 2:1 mixture of two isomers, and computer simulated analysis[33] using chemical shifts and coupling constants for substituted cyclopentadienes[34] shows that the major and minor isomers are the 1-aryl-3-alkyl- and 1-aryl-4-alkylcyclopentadienes, respectively. Conversion of **11a** to a mixture of diastereomeric ferrocenes **12a** in 72% yield was readily achieved by treatment with sodium hexamethyldisilylamide followed by anhydrous ferrous chloride. Finally, coupling of **12a** with an excess of CpCuSMe$_2$ gave the effective monomer **13a** (98%).[35]

Polymerization of **13a** was carried out in THF solution by treatment with NaN(SiMe$_3$)$_2$ at 0 °C, fol-

Chart 1



14

a. M=Fe, R=R'=H
b. M=Fe, R=2-octyl, R'=H
c. M=Fe, R=R'=2-octyl
d. M=Fe, R=3,7-dimethyloctyl, R'=H
e. M=Fe, R=n-decyl, R'=H
f. M=Ni, R=R'=H
g. M=Ni, R=2-octyl, R'=H
h. M=Ni, R=R'=2-octyl
i. M=Co, R=2-octyl, R'=H

lowed by the addition of anhydrous $FeCl_2$ at room temperature. The reaction, which is slow under these conditions, was allowed to proceed for a period of 10 days. In several of the runs we noted that the addition of small amounts of $FeCl_2$ and especially of base was needed to promote further polymerization. This is most likely due to the adventitious introduction of traces of water, which on the small scale of the reaction would be sufficient to quench the cyclopentadienyl anion end groups and hydrate the ferrous salt. The presence of reactive end groups in the polymer is evidenced by the observation that resubmission of an isolated low molecular weight polymer sample ($M_w = 6500$, $M_n = 3360$) to further reaction with base and $FeCl_2$ led to polymer growth and the formation of a polymer fraction (49%) with $M_w = 12\,800$ and $M_n = 5200$.[36]

The toluene-soluble portion of the crude product polymer was further purified by extraction with ether and then methanol to remove lower molecular weight material and unreacted $FeCl_2$. This left a dark purple solid (72% yield), which was also soluble in benzene and in THF. A GPC analysis of the polymer **14b** (Chart 1) gave $M_n = 14\,360$ and $M_w = 18\,400$ and showed a bimodal peak distribution with peak maxima at 26 600 and 16 000.

Since calibration of the GPC was made using polystyrene standards, while polymers of structure **14** are relatively rigid, we considered it important to have an independent measure of molecular weight. This was carried out by end-group analysis using proton NMR data for a sample of **14b.** The proton NMR spectrum of this material showed very broad resonance signals centered at δ 7.3, 6.0, 3.8, and 1.1 corresponding to aromatic, terminal cyclopentadienyl, ferrocenyl, and aliphatic protons, respectively. End-group analysis was carried out by comparing integrated areas for vinyl protons of the terminal cyclopentadienyl rings with those areas for aryl or for ferrocenyl plus aliphatic proton signals. These measurements gave values of $M_n = 18\,000$ and 17 700, respectively, and served to corroborate the molecular weight measurement determined by GPC analysis. A similar comparison of GPC and end-group analyses was carried out on the ferrocene–nickelocene copolymer **14f**, which gave GPC values of $M_n = 1790$ and $M_w = 2970$, compared with end-group values of 2530 (aryl/vinyl), 2640 (aryl/$CpCH_2$), 2210 (ferrocenyl/vinyl), and 2280 (ferrocenyl/$CpCH_2$).

The presence of intact ferrocene units within polymer **14b** is further evidenced by the appearance of strong absorption at 820 and 440 cm^{-1} in the infrared spectrum of this material, assignable to C–H out-of-plane and metal–ring stretching vibrations of ferrocene, respectively.[37]

The effect of other hydrocarbon chains and of further substitution of the monomer on the course of polymerization and on the solubility of the product was briefly examined. Monomer **13c**, in which all four of the cyclopentadienyl rings are substituted by a 2-octyl chain, was prepared in 93% yield by treatment of **12a** with excess alkylcyclopentadienylcopper reagent. Polymerization of this material by reaction with sodium hexamethylsilylamide and ferrous chloride took place slowly in refluxing THF and yielded polymer **14c**, which on fractionation gave a dark purple polymer in 50% yield. This material was insoluble in benzene, and hot toluene, and only slightly soluble in THF. GPC analysis of the polymer which partially (<10%) dissolved in THF showed a bimodal peak distribution, with the major peak at 4700 and a minor component peak at 136 000. Thus, further alkylation of the monomer has the desired effect of keeping the growing polymer in solution and allowing a higher degree of polymerization to be achieved, but the resulting fractionated product is relatively insoluble in common organic solvents.

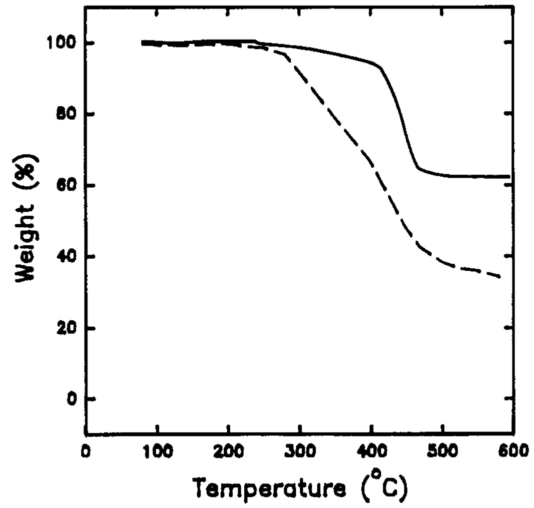


Figure 2. Thermogravimetric curves for polymers **14d** (—) and **14b** (– –). N_2 purge, ramp 20 °C/min.

In order to examine the effect of chain branching on polymer crystallinity, (3,7-dimethyloctyl)cyclopentadiene was prepared, by catalytic hydrogenation of citral, followed by condensation of the saturated aldehyde with cyclopentadiene and reduction of the fulvene with lithium aluminum hydride. Conversion to the complex copper salt and coupling with diiodonaphthalene gave **11b** (46%). This was converted, as before with **11a**, to the ferrocene **12b** (50%) and hence to the monomer **13b** (88%). Polymerization in refluxing THF was relatively slow and yielded polymer **14d** with $M_w = 10\,640$ and $M_n = 4600$ as a dark red solid (48%), which was soluble in THF at room temperature. Similarly, *n*-decylcyclopentadiene was converted to the monomer **13d** and polymerized at room temperature over a period of several days to give a benzene-soluble fraction **14e** in 70% yield with $M_w = 16\,300$ and $M_n = 8100$.

Thermal Behavior. The TGA thermogram for a sample of polymer **14d** ($M_w = 10\,600$ and $M_n = 4600$), shown in Figure 2, exhibits an onset of decomposition at 416 °C, with a relative residual weight of 65% at 465 °C, reflecting its relatively high thermal stability, which is similar to that observed in poly(ferrocenylene) polymers.[38] By contrast, the TGA curve for a sample of polymer **14b** ($M_w = 13\,000$, $M_n = 4500$) (Figure 2) shows a two-step decomposition curve with a much lower onset decomposition temperature of 287 °C, but with a second higher temperature decomposition step, in the same temperature region as observed for polymer **14d**. It

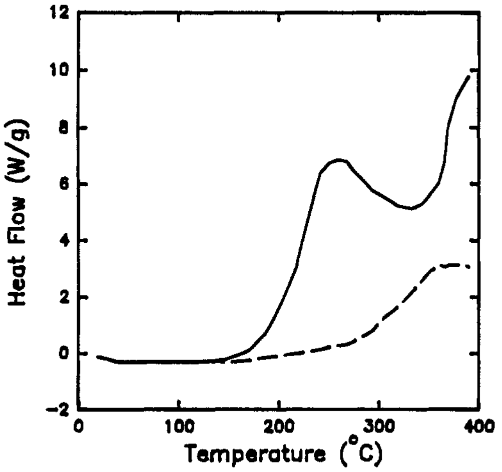


Figure 3. Differential scanning calorimetric curves for **14d** (—) and a sample of **14b** lacking Cp end groups (– –). N_2 purge, ramp 20 °C/min.

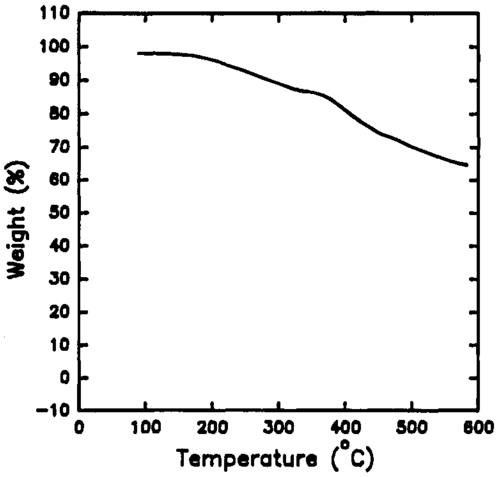


Figure 4. Differential scanning calorimetric curve for **14f**. N_2 purge, ramp 20 °C/min.

Table 1. Conductivity of Doped Polymers 14a,b

% oxidation[a]	σ (S/cm)[b]
14b (M_w = 18 400, M_n = 14 400)	
37	2.5×10^{-4}
37	6.7×10^{-3} [c]
67	1.4×10^{-5}
14b (M_w = 12 900, M_n = 3 750)	
0	$<10^{-12}$
20	2.7×10^{-8}
50	5.3×10^{-7}
14a (M_w = 2540, M_n = 1830)	
22	5.4×10^{-5}
31	8.6×10^{-5}
37	1.0×10^{-4}
54	4.3×10^{-5}
74	2.4×10^{-5}

[a] By treatment of methylene chloride solutions of polymer with standard solutions of iodine in benzene solution at room temperature. [b] Two-probe dc measurement. [c] Four-probe measurement.

seems likely that the decomposition pathway for polymer **14b** is associated with thermolytic scission of the side-chain carbon to the cyclopentadienyl ring bond and that the lower onset temperature for this polymer reflects the lower bond energy of the 2 °C−ring bond of the side chain in this polymer compared with the 1 °C−ring bond in **14d**.[39] Alkyl group cleavage, coupled with the higher temperature decomposition, associated with rupture of the Fe−Cp ring bond, would then lead to a higher overall weight loss. The DSC thermogram for **14d** (Figure 3) exhibits a strong exotherm (915 J/g) at 250 °C, characteristic of a secondary polymerization reaction.[40] Since the polymer is likely to have free cyclopentadienyl end groups, further polymerization through Diels−Alder reactions of these end groups is possible. Some support for this view is derived from the DSC behavior of a sample of polymer **14b**, which had been recovered from a polymerization reaction and had then been resubmitted twice to further polymerization by treatment with base and ferrous chloride, without significant change in molecular weight. The failure of this substance to undergo further chain growth suggests that it lacks cyclopentadienyl end groups. In conformity with this conclusion, the DSC thermogram of this polymer was featureless throughout the temperature region in which **14d** showed a strong exotherm.

The iron−nickel copolymer **14f**, which lacks side-chain substitution of the cyclopentadienyl rings, exhibits a distinct two-step thermogravimetric analysis decomposition curve (Figure 4), reflecting the marked difference in the dissociation energies of ferrocene and nickelocene of 73 and 60 kcal/mol, respectively.[41]

Charge Transport. The dc electrical conductivity of partially oxidized **14a,b** and the dependence of conductivity on polymer molecular weight and degree of oxidation were examined. Samples of these polymers were oxidized in a methylene chloride solution by treatment with iodine. The partially oxidized material, which precipitated from solution as a brown or black solid, was collected and its conductivity was determined as a compressed pellet by a two- or four-probe measurement. These results are summarized in Table 1.

It is important to note that the oxidation levels given in the table are nominal. These are calculated from the amount of I_2 used relative to the moles of ferrocene units in the polymer sample and are based on the stoichiometry defined in eq 1, which has been shown to hold for ferrocene itself. This stoichiometry derives from the circumstance that, although conversion of ferrocene by iodine to ferrocenium and iodide (eq 2) is a thermodynamically unfavorable step,[42] the oxidation, nevertheless, proceeds due to the very favorable enthalpy change associated with the conversion of iodide to triiodide (eq 3).[43] The free-energy change for reaction 2 may be estimated to be +1.7 kcal/mol from the formation constant of triiodide (eq 3; $K_a = 10^7$)[44] and from the free-energy change measured for eq 1 of −2.52 kcal/mol.[45] We had earlier observed[10] that the cyclic voltammetric half-wave oxidation potentials for the iron oligomers **3a** show a progressive decrease with increasing chain length. For example, the first oxidation potential for **3a** (n = 2) is 0.09 V lower than the corresponding potential for the dinuclear compound **3a** (n = 1), while the second oxidation potentials for these compounds differ by 0.13 V. A further, but smaller, decrease in the first and second oxidation potentials is observed for **3a** (n = 3) compared with **3a** (n = 2). Reaction 2 should therefore be more favorable for the corresponding polymer **14a** and especially for alkylated polymer **14b** polymer, since alkylation of ferrrocene generally results in a decrease in oxidation potential.[46] Hence, the effective average degree of oxidation of the bulk polymer is likely to be greater than indicated in the table. This conclusion is supported as well by Mössbauer experiments on samples of doped polymer (*vide infra*) and by an analysis of the electronic spectrum of a polymer sample of **14b** (M_w = 12 900 and M_n = 3750), with a nominal oxidation level of 20%. Based on a Beer's law

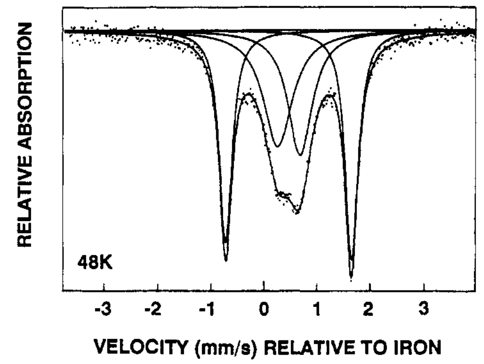


Figure 5. Mössbauer spectrum of (1,8-diferrocenylnaphthalene)$^+$ BF_4^- at 48 K.

plot for ferrocenium tetrafluoroborate at $\lambda_{max} = 616$ nm and correcting for the much smaller absorption by the neutral polymer at this wavelength, this sample was analyzed for a doping level of 40%, which is intermediate between that calculated on the basis of the stoichiometries of eqs 1 and 2.

$$2Cp_2Fe + 3I_2 \rightleftharpoons 2Cp_2Fe^+ + 2I_3^- \quad (1)$$

$$Cp_2Fe + I_2 \rightleftharpoons Cp_2Fe^+ + 2I^- \quad (2)$$

$$I^- + I_2 \rightleftharpoons I_3^- \quad (3)$$

As a consequence, the doping process is likely to be inhomogeous, resulting in the formation of iodide and triiodide and a dependence of the doping level on polymer chain length.

The limited data of Table 1 also suggest that polymer chain length is not an important factor in charge transport in the stacked iron polymers. The absence of a significant intervalence absorption band in the parent monocation **3a**$^+$ ($n = 1$),[47] shows it to be a weakly interacting mixed-valence system, and consequently the band structure of the derived polymer would be expected to favor localized electronic states. The mode of electron transport in polymer **14** (M = Fe), as in poly(1,1'-ferrocenylene)[48] and structurally related poly(vinylferrocene) and poly(ethynylferrocene) polymers,[49] is likely to involve a phonon-assisted hopping mechanism between Fe^{2+} and Fe^{3+} paired centers.[50] This conclusion is consistent as well with the bell-shaped curve dependence of conductivity on oxidation level, which has also been observed in poly(vinylferrocene) and poly(ethynylferrocene) polymers.[49] Although the conductivities observed for partially oxidized samples of polymer **14a,b** lie well within the semiconductor range, it is of interest to note that the highest conductivity observed for a sample of **14b** of 6.7×10^{-3} S/cm is almost 2 orders of magnitude above that recorded for an iodine-doped, partially crystalline sample of poly(1,1'-ferrocenylene).[48] Furthermore, the temperature-dependent conductivity of this material showed essentially no change in conductivity between 300 and 15 K.

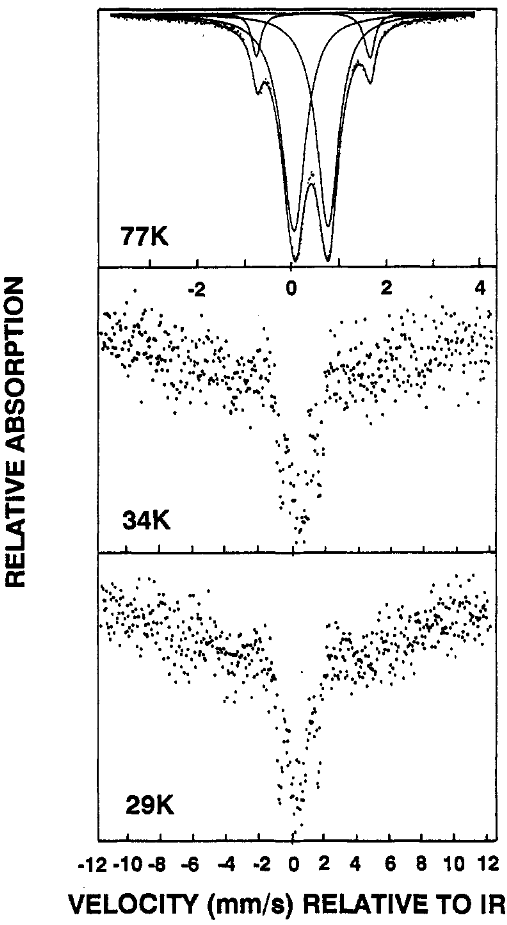


Figure 6. Mössbauer spectrum of polymer **14b** $M_w = 18\,400$ and $M_n = 14\,400$, oxidized to a nominal level of 37% with I_2) in the temperature range of 77–29 K.

Mössbauer Spectra. 1,8-Diferrocenylnaphthalene **3a** ($n = 1$) exhibits a typical ferrocene-like[51] Mössbauer spectrum for which the isomer shift δ and quadrupole splitting ΔE are 0.44 (relative to iron metal) and 2.40 mm/s, respectively, at ambient temperature. The spectrum of **3a** monocation, recorded at 48 K (Figure 5), indicates trapped low-spin Fe(II) and Fe(III) valence states,[52] which remain so up to ambient temperature for both the BF_4^- and I_3^- salts. The spectra of several samples of polymer **14b**, oxidized to different levels, also suggest trapped valence states. Typical spectra for a polymer sample with $M_w = 18\,400$ and $M_n = 14\,400$ and oxidized to a nominal level of 37% with iodine are shown in Figures 6 and 7. At 77 K the intense central low-spin doublet is broadened as the result of a range of molecular environments in combination with incipient, single ion, slow paramagnetic relaxation effects. With decreasing temperature, *progressive,* slow paramagnetic relaxation is apparent in the "winglike" base-line shape (Figure 6) and in the ultimately resolved nuclear Zeeman splitting (Figure 7, bottom). These systems are apparently sufficiently self-diluted (Fe(III)...Fe(III) distances ≥ 5 Å) so as to give rise to long spin–spin relaxation times, but, at the same time, decreasing temperature leads to an increase in spin-lattice relaxation time. The intensity of the rapidly relaxing Fe(III) fraction is seen to decrease dramatically but not quite vanish between 17 and 4.6 K (see arrow in Figure 7, bottom). We note that, within this temperature range, the observed hyperfine splitting effects are not characteristic of cooperative magnetic order.[53]

Instead, the limiting spectrum at 4.6 K exhibits a central doublet characteristic of a diamagnetic (ferrocene-like) Fe(II) fraction superimposed on a broad magnetic hyperfine split background corresponding to low-spin Fe(III) in the infinitely long relaxation time limit. The value of the internal field is very large (~48.4 T) compared with that expected (11 T) for a spin-only Fermi contact contribution for a nominal spin-doublet single ion ground state. Such unexpectedly large values

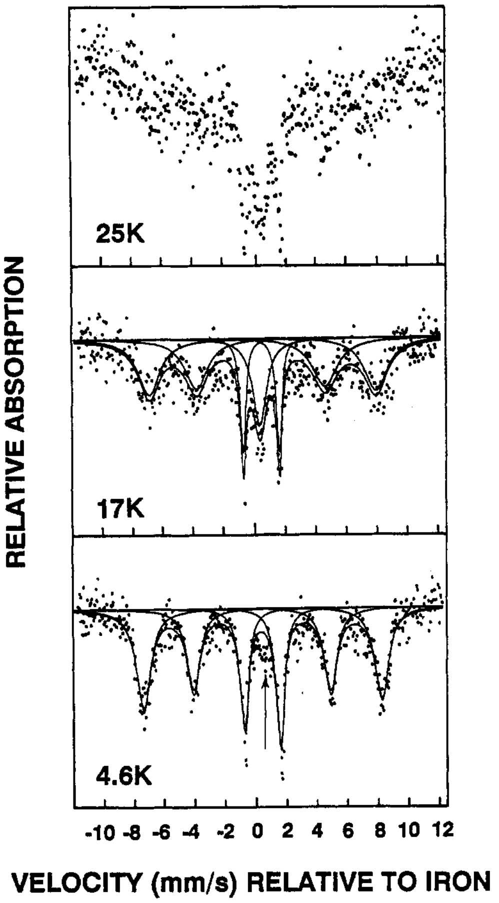


Figure 7. Mössbauer spectrum of polymer **14b** (M_w = 18 400 and M_n = 14 400, oxidized to a nominal level of 37% with I_2) in the temperature range of 25–4.6 K.

of the internal field have been previously[54] observed for low-spin Fe(III) systems having a substantial orbital contribution to the internal field and in the limit of extreme *g*-factor anisotropy ($\Delta g \sim 1.5$). Finally, the limiting 4.6 K spectrum of the polymer with a nominal oxidation level of 37% suggests that the actual level of oxidation is considerably greater than this. At this temperature, at which the recoil-free fractions of the Fe(II) and Fe(III) sites are expected to be most similar, the spectrum suggests a lower oxidation limit of ~70% for this material.

Mixed-Metal Polymers. It is apparent that ferrocene compounds **8** and **13** may in principle, serve as monomers for the construction of bimetallic polymers **14**, in which ferrocene alternates with other metallocenes along the chain. In practice, treatment of **8** in a THF solution successively with sodium hexamethylsilylamide at −78° and then with nickel acetylacetonate at room temperature for 24 h yielded a polymeric product, which was fractionated by extraction with ether, toluene, and methanol to remove lower molecular weight components and unreacted nickel acetylacetonate. The remaining polymeric product **14f**, obtained in 54% yield as a dark purple solid, was only partially soluble in THF solution. GPC analysis of the THF-soluble portion of this material showed a broad envelope with M_n = 1790 and M_w = 2970 and a bimodal peak distribution, indicating the presence of a small component of less soluble polymer of much higher molecular weight (peak at 30 000). Owing both to its polymeric nature and to the presence of a paramagnetic metal center, the proton NMR spectrum of this material showed very broad resonances centered at δ 7.5. 6.0, 4.4, and 2.6 corresponding to aromatic, vinyl, ferrocenyl, and methylene protons in the end group, respectively. An end-group analysis of this product was carried out by measuring the ratio of integrated areas for aromatic or ferrocenyl proton resonances to terminal cyclopentadienyl-vinyl or methylene signals. This gave an average value of M_n = 2400 for the polymer, in modest agreement with the GPC analysis.

As anticipated, cyclopentadienyl protons in the nickelocene unit of the copolymer exhibit large contact shifts owing to transfer of positive spin density from the paramagnetic metal to the ring carbon atoms.[55] Resonances observed for α and β protons of the monosubstituted cyclopentadienyl ring are centered at δ −262, a value close to that observed for ring protons of nickelocene itself (δ −254.8,[56] line width at half-height = 5.5 ppm).[57] Since molecular tumbling is restricted in the polymer, electron spin–lattice relaxation time is not as short as in 1,1′-dimethylnickelocene,[52] and consequently the separate signals for α and β cyclopentadienyl ring protons are observed as overlapping triplets (line width at half-height = 3.5 ppm) in this mixed-metal polymer.

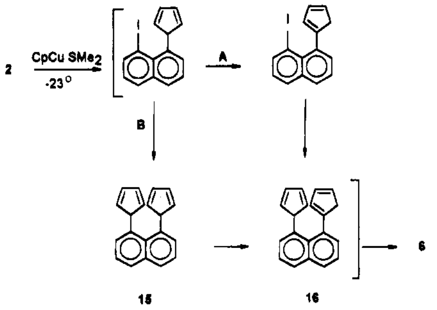
Similar use of bis(cyclopentadienide) salts derived from di- and tetraalkylated monomers **13a** and **13c** in polymerization reactions with nickel(II) salts was briefly examined. While these monomers gave iron–nickel polymers of apparently higher molecular weight, the bulk of the product, obtained as a dark purple solid, was found to be largely insoluble in common solvents and was therefore difficult to characterize. A GPC trace of the THF-soluble portion of the fully alkylated polymer **14h** showed a broad envelope with M_n = 1,500 and M_w = 5700, with a significant proportion of material between the range of 18 000 and 30 000 molecular weight. Alkylation of the cyclopentadienyl ring in these mixed-metal polymers appears to have a lower solubilizing effect on the fractionated product than was observed for the all-iron polymers.

The presence of intact nickelocene units in these polymers is further evidenced by absorptions at 390 and 440 cm^{-1} in the infrared spectrum of **14g**. The first is close to the absorption at 355 cm^{-1} in nickelocene, assigned to a ring–metal stretching vibration,[58] while the second corresponds to a similar vibration in ferrocene, which gives rise to absorption at 478 cm^{-1}.[59]

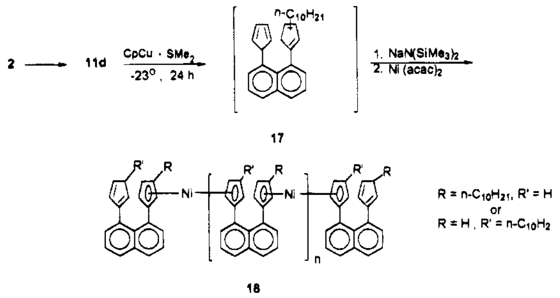
A preliminary examination of possible cooperative magnetic behavior within the polymer was made by determining the bulk magnetic susceptibility of a sample of polymer **14g**. Measurements were carried out at room temperature on a Faraday susceptibility balance and gave a mean effective moment of 3.51 μ_B, a value higher than the moment of 2.89 μ_B observed for nickelocene itself.[60]

Polymer **14i** incorporating alternating ferrocene and cobaltocene units was also prepared from **13b** dianion by reaction with $CoCl_2$. The reaction was allowed to proceed for several days at room temperature, and the crude product was fractionated by exhaustive extraction with THF, leaving behind a black, shiny solid in 80% yield. As before, the presence of both cobaltocene and ferrocene nuclei in the polymer is evidenced by its infrared spectrum, taken in CsI, which shows absorptions at 450 and 380 cm^{-1}, characteristic of the ring–metal stretching modes in ferrocene and cobaltocene (355 cm^{-1}).[61] Bulk susceptibility measurements on this polymer sample gave a mean effective magnetic moment of 5.2 μ_B, a value considerably greater than that

Scheme 5



Scheme 6



observed for cobaltocene itself, which shows an effective moment of 1.7 μ_B.[62,63]

A proton NMR spectrum of the THF-soluble, lower molecular weight material, obtained from the polymerization reaction, showed, as anticipated, very broad resonances centered at δ 7.5, 5.3, 3.5, 2.2, and 1.0 corresponding to aromatic, vinyl, ferrocenyl, methylene, and aliphatic protons, respectively. At higher field, a short acquisition time, rapid-recycle NMR experiment[57] showed resonances for α and β ring protons in the cobaltocene units of the polymer as two overlapping doublets centered at -66 ppm (width at half-height = 13 ppm). The protons in cobaltocene itself show resonance at δ -53.8 ppm.[64]

Nickelocene-Based Polymers. The general methodology used for the preparation of mixed-metal Fe–Ni and Fe–Co polymers is unsuited to the synthesis of a broader structural range of metallocene polymers, especially those lacking a ferrocene core. Thus, an attempt to prepare the nickelocene analog of **7** by reaction of **4** with base followed by nickel salts was unsuccessful. By contrast, the cobaltocene and cobaltocenium analogs of **7** could be prepared, but attempts to convert these to the cobalt analog of **8** also proved fruitless.[65] We therefore sought a general route to this class of compound.

In a separate investigation, we had shown that the coupling reaction of cyclopentadienylcopper–dimethyl sulfide with 1,8-diiodonaphthalene (**2**), which yields the Diels–Alder product **6**, proceeded by path B (Scheme 5) rather than the closely parallel path A.[66] Since intermediate **15** is stereochemically incapable of undergoing intramolecular cycloaddition, we were led to consider that it might be trapped, providing that its conversion to **16** was sufficiently slow at −23 °C.

In order to examine this prospect, cyclopentadienylcopper–dimethyl sulfide and diiodonaphthalene (**2**) were allowed to react at −23 °C for 24 h until consumption of the diiodide was complete, and the solution was then treated with base and ferrous chloride. The resulting product was fractionated by solubility and shown to be a mixture of benzene-insoluble polymer and lower molecular weight, benzene-soluble polymer **14a**. However, an attempt to effect this reaction sequence using either *n*-decyl- or 2-octylcyclopentadienecopper–dimethyl sulfide in place of the unsubstituted cyclopentadienide was unsuccessful. Instead, the coupling reaction stopped cleanly at the the monosubstitution product stage to give **11a** or **d**, even in the presence of excess copper reagent. Nevertheless, we found that **11d**, which had undergone sigmatropic change in the course of its isolation, could be resubmitted successfully to a coupling reaction with unsubstituted cyclopentadienylcopper–dimethyl sulfide at −23 °C. Surprisingly, the bis(cyclopentadienyl)ated product **17** (Scheme 6), which unlike **15** is capable of undergoing intramolecular cycloaddition, could also be trapped by treatment of the reaction mixture with base and ferrous chloride. The resulting material, on fractionation yielded ferrocene polymer with a GPC peak at $M \simeq 15\,000$.

When this reaction was run again and intermediate **17** was trapped by treatment of its dianion with Ni(acac)$_2$, a THF-soluble polymer **18** was isolated as a black solid in low yield. GPC analysis of this material gave $M_n = 3700$ and $M_w = 6600$ corresponding to a polymer with 8–15 nickelocene units. The presence of nickelocene nuclei in the polymer is supported by intense absorption at 797 cm^{-1} in its infrared spectrum, associated with the superposition of C–H out-of-plane bending modes of nickelocene[55] and naphthalene.[67] Further evidence for this structure is provided by the far-infrared spectrum of the polymer, which shows a single band at 360 cm^{-1}, close to a metal–ring stretching band observed in nickelocene at 355 cm^{-1}. As anticipated, the absorption at 480 cm^{-1}, observed in **14f**, is absent in **18**. The very dark color of the polymer is due to long tail absorption throughout the visible region. In addition, this material shows absorption maxima at 230 and 300 nm, similar to that found in nickelocene.[68]

Preliminary examination of the magnetic properties of this polymer was carried out by measurement of the bulk magnetic susceptibility of this material. The value of the magnetic moment of 5.3 μ_B is very much higher than that observed for nickelocene itself of 2.89 μ_B. Further study of the temperature dependence of the magnetic properties of this and other metallopolymers of this class, based on spin unpaired metallocenes, is planned.

In contrast to the mixed iron–nickel polymer **14f**, we were unable to detect a high-field resonance for the all-nickel polymer **18**, even under conditions of a short acquisition time and rapid-recycle NMR experiment.

Conclusion

We have outlined the evolution of synthetic methodologies used in the construction of a new class of organometallic polymer, composed of metallocene units held in a stacked configuration. The preparation of all-ferrocene and all-nickelocene polymers as well as mixed iron–nickel and iron–cobalt polymers has been achieved. The methods available for the synthesis of these materials has now evolved to the point at which the preparation of a much broader class of stacked polymeric complexes, based on cyclopentadiene, can be envisioned. The synthesis of these and a study of their chemical, electrical, magnetic, and optical properties remain to be accomplished.

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