Synthesis and Properties of New Stacked Metallocene Polymers

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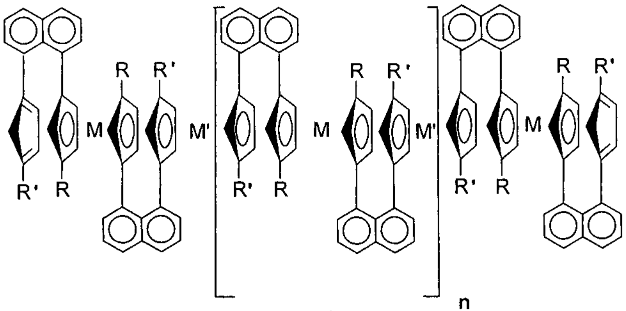
The substituted cyclopentadienes **5a**,**b** are readily prepared in two steps from benzyloxybenzaldehyde and 4-dimethylaminobenzaldehyde by condensation with cyclopentadiene followed by lithium aluminum hydride reduction of the fulvenes **4a**,**b**. Coupling of the zinc salts of **5a**,**b** with 1,8-diiodonaphthalene in the presence of a catalytic amount of CuI gives the cyclopentadienylated iodonaphthalenes **6a**,**b**. This new protocol represents a significant improvement over earlier procedures for the preparation of such compounds. Conversion of **6a**,**b** to the ferrocenes **7a**,**b**, followed by a second cyclopentadienylation step, affords **8a**,**b** or **9a**. These serve as monomers for the synthesis of polymers **1d**,**e** and copolymers **1f**−**h**. These materials show increased molecular weights and improved solubility compared with **1b**,**c** and analogues, in which the cyclopentadienyl-ring substituents are alkyl chains.

Introduction

The design and synthesis of macromolecules that incorporate transition metals or transition metal complexes as essential structural elements constitutes an area of growing research interest, promoted largely by the prospect that such materials may possess novel optical, redox, magnetic, or electrical properties.[1] Several members of this class have thus far been shown to exhibit liquid crystal behavior[2] and significant nonlinear optical[3] properties.

We recently reported the preparation of the first members of a structurally unique class of organometallic polymer **1** in which the component metallocene units are constrained to a face-to-face, stacked arrangement, through their peri-substitution on a naphthalene spacer.[4] Owing to the restricted degrees of freedom within these columnar metallocene polymers, they behave as rigid rod type polymers,[5] and consequently their solubility in common organic solvents is poor. In our earlier paper, we examined the effect of long chain alkyl substituents in the monomer on the properties of the resulting polymer and observed a measure of improvement in both polymer size and solubility. In the present paper we report the preparation and polymerization of several aryl-substituted monomers and a further improvement in the general methodology for monomer synthesis.



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Experimental Section

General Procedures and Chemicals. Reactions were carried out using standard Schlenk techniques under an argon atmosphere. Tetrahydrofuran was freshly distilled from sodium benzophenone ketyl, and pyridine was stored over 4 Å molecular sieves before being distilled from CaH under an argon atmosphere. Anhydrous dimethoxyethane[6] was used as received.

Elemental analyses were performed by QTI Co, Salem, NJ, and by Desert Analytics, Tucson, AZ. HPLC analyses were carried out using a system incorporating a Waters model 410 automated gradient controller, a model 510 pump, a model U6-K injector, a model 401 refractive index detector, a Waters 746 data module, and Waters Ultrasytragel columns (10^4 and 500 Å). HPLC grade pyridine was used as received and run at 0.8 mL/min. A calibration curve for gel permeation analysis

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[1] Chisholm, M. H. *Angew. Chem., Int. Ed. Engl.* **1991**, *30*, 673−674, and references therein. Pittman, C. U.; Carraher, C. E.; Zeldin, M.; Sheats, J. E.; Culbertson, B. M. *Metal-Containing Polymeric Materials*; Plenum: New York, 1996. Manners, I. *Angew. Chem., Int. Ed. Engl.* **1996**, *35*, 1602−1621, and references therein. Buretea, M. A.; Tilley, T. D. *Organometallics* **1997**, *16*, 1507−1510. Nguyen, P.; Lough, A. J.; Manners, I. *Macromol. Rapid Commun.* **1997**, *18*, 953−959. Gomez-Elipe, P.; Macdonald, P. M.; Manners, I. *Angew. Chem., Int. Ed. Engl.* **1997**, *16*, 762−764. Yamamoto, T.; Morikita, T.; Maruyama, T.; Kubota, K.; Katada, M. *Macromolecules* **1997**, *30*, 5390−5396. Cardona, C. M.; Kaifer, A. E. *J. Am. Chem. Soc.* **1998**, *120*, 4023−4024, and references therein. Rehahn, M. *Acta Polym.* **1998**, *49*, 201−224, and references therein.

[2] Takahasi, S.; Takai, Y.; Morimoto, H.; Sonogashira, K.; Hagihara, K. *Mol. Cryst. Liq. Cryst.* **1982**, *82*, 139. Abe, A.; Kimura, N.; Tabata, S. *Macromolecules* **1991**, *24*, 6238.

[3] Frazier, C. C.; Guha, S.; Chen, W. P.; Cockerham, P. L.; Porter, P. L.; Chauchard, E. A.; Lee, C. H. *Polymer* **1987**, *28*, 553. Kanis, D. R.; Ratner, M. A.; Marks, T. J. *J. Am. Chem. Soc.* **1990**, *112*, 8203−8204, and references therein. Kanis, D. R.; Ratner, M. A.; Marks, T. J. *Chem. Rev.* **1994**, *94*, 195−242. Long, N. J. *Angew. Chem., Int. Ed. Engl.* **1995**, *34*, 21−38.

[4] Rosenblum, M.; Nugent, H. M.; Jang, K.-S.; Labes, M. M.; Cahalane, W.; Klemarczyk, P.; Reiff, W. M. *Macromolecules* **1995**, *28*, 6330−6342, and references therein.

[5] Ballauff, M. *Angew. Chem., Int. Ed. Engl.* **1989**, *28*, *253*-267.

[6] Aldrich Chemical Co., Milwaukee, MI.

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of polymers **1d**−**h** in pyridine solution was established using polystyrene standards in the same solvent. Polymers reported in Tables 2 and 3 were found to be partially soluble in pyridine, but insoluble in THF. The use of polystyrene standards in these determinations finds support in the correlation of GPC-derived M_n values, using these standards, with those derived from end group analysis for the closely related alkyl-substituted polymers.[4]

Zinc chloride[6] (98%) was dried with TMSCl according to the method of So and Boudjouk[7] and heated to just below the melting point under vacuum prior to use. $FePy_4(SCN)_2$,[8] $Ni(NH_3)_6Br_2$,[9] $NiBr_2$·2DME,[10] and $NiCl_2$·2THF[11] were prepared according to the literature. $FeCl_2$ (anhydrous beads, ∼10 mesh, 99.9%)[6] was used as received. 1,8-Diiodonaphthalene was prepared according to the procedure of House[12] from commercially available 1,8-diaminonaphthalene.[6] The crude product was obtained as light brown crystals and was further purified by sublimation and recrystalization to afford yellow crystals, mp 109−110 °C. All other chemicals and reagents were used as received without further purification.

6-(4-Benzyloxyphenyl)fulvene (4a). Following the procedure of Stone and Little,[13] pyrrolidine (2.13 g, 30.0 mmol) was added to a solution of 4-benzyloxybenzaldehyde (5.00 g, 23.6 mmol) and freshly cracked cyclopentadiene (3.17 g, 48 mmol) in MeOH (24 mL). A thick orange precipitate formed after a few minutes, and stirring was continued overnight. An aqueous solution of acetic acid (2 mL in approximately 50 mL of water) was added, and the mixture was extracted with diethyl ether (3 × 100 mL). The extracts were combined and washed with water (2 × 100 mL) and brine (50 mL) before being dried over $MgSO_4$. The solvent was removed in vacuo, and the residue was purified by flash chromatography on silica gel (30:70 diethyl ether/hexanes) to afford **4a** as a red solid (5.78 g, 95%). IR (KBr): 2908, 1600, 1509, 1466, 1348, 1258, 1175, 1003, 820, 759, 745, 696, 618 cm^{-1}. ^1H NMR (300 MHz, $CDCl_3$): δ 5.11 (s, 2 H, OCH_2Ph), 6.32 (m, 1 H, Cp−*H*), 6.49 (m, 1 H, Cp−*H*), 6.67 (m, 1 H, Cp−*H*), 6.73 (m, 1 H, Cp−*H*), 7.01 (d, $J = 9.2$ Hz, 2 H, Ar−*H*), 7.17 (s, 1 H, Cp=C*H*), 7.40 (m, 4 H, Ar−*H*), 7.58 (d, $J = 8.6$ Hz, 2 H, Ar−*H*). ^{13}C NMR (100.5 MHz, $CDCl_3$) δ 70.2, 115.3, 120.1, 127.6, 127.7, 128.3, 128.8, 129.95, 130.0, 132.7, 135.2, 136.7, 138.4, 143.6, 160.0. Anal. Calcd for $C_{19}H_{16}O$: C, 87.7; H, 6.2. Observed: C, 87.5; H, 6.2.

6-(4-Dimethylaminophenyl)fulvene (4b). The same procedure as above was followed with 4-dimethylaminobenzaldehyde (4.00 g, 26.8 mmol), pyrrolidine (2.92 g, 41.1 mmol), and freshly cracked cyclopentadiene (4.51 g, 68.5 mmol) in MeOH (27 mL). The mixture was stirred overnight and worked up as above to afford **4b** as an orange solid after chromatography (silica gel, 30:70 diethyl ether/hexanes) (4.87 g, 92%). IR (KBr): 2896, 1597, 1525, 1370, 1346, 1233, 1197, 909, 815, 756, 622 cm^{-1}. ^1H NMR (300 MHz, $CDCl_3$): δ 3.00 (s, 6 H, $N(CH_3)_2$), 6.33 (m, 1 H, Cp−*H*), 6.43 (m, 1 H, Cp−*H*), 6.62 (m, 1 H, Cp−*H*), 6.67 (d, $J = 7.0$ Hz, 2 H, C*H*C(NMe$_2$)C*H*), 6.79 (m, 1 H, Cp−*H*), 7.12 (s, 1 H, Cp=C*H*), 7.56 (d, $J = 7.0$ Hz, 2 H, C*H*C(CH=Cp)C*H*). ^{13}C (100.5 MHz, $CDCl_3$): δ 40.0 ($N(CH_3)_2$), 111.8 (C9), 119.4 (C1), 124.6 (C7), 127.5 (C4), 128.0 (C3), 132.7 (C8), 133.6 (C2), 139.8 (C6), 140.7 (C5), 151.0 (C10). Anal. Calcd for $C_{14}H_{15}N$: C, 85.3; H, 7.6; N, 7.1. Observed: C, 85.2; H, 7.6; N, 6.9.

4-Benzyloxybenzyl-1- and 2-cyclopentadiene (5a). Following the procedure of Hafner[14] a flame-dried flask was charged with LAH (0.304 g, 8.0 mmol), and dry diethyl ether (15 mL) was added. A solution of **4a** (0.988 g, 3.8 mmol) in dry diethyl ether (15 mL) was added dropwise, and this was accompanied by vigorous effervescence. The solution was stirred for a further 1 h, after which time the characteristic yellow fulvene color had been discharged. The gray suspension was transferred to a large conical flask cooled in an ice/water bath, and cold methanol (10 mL) was added dropwise (CAUTION!) followed by 2 N HCl (30 mL), causing the solution to separate into two clearly defined phases. The mixture was extracted with diethyl ether (2 × 50 mL), and the combined organic portions were washed with water (2 × 100 mL) and brine (50 mL). The solvent was removed in vacuo, and the residue was purified by flash chromatography on silica gel (30:70 diethyl ether/hexanes) to afford **5a** as a pale yellow oil and as an inseparable mixture of isomers in the ratio 1:1. ^1H NMR (400 MHz, $CDCl_3$): δ 2.84 (m, 2 H, CHC*H*$_2$CH, isomer A or B), 2.96 (m, 2 H, CHC*H*$_2$CH, isomer A or B), 3.63 (br s, 2 H, CHC*H*$_2$CH isomer A or B), 3.67 (br s, 2 H, CpC*H*$_2$, isomer A or B), 5.03 (s, 4H, C*H*$_2$Ph, isomer A and B), 5.98 (m, 1 H, C*H*, isomer A or B), 6.12 (m, 1 H, *CH*, isomer A or B), 6.24 (m, 1 H, *CH*, isomer A or B), 6.39 (m, 3 H, *CH*, isomer A and B), 6.89 (m, 4 H, Ar−H, isomer A and B), 7.10 (m, 4 H, Ar−H, isomer A and B), 7.44−7.30 (m, 10 H, Ar−H, isomer A and B). Anal. Calcd for $C_{19}H_{18}O$: C, 87.0; H, 6.9. Observed: C, 86.9; H, 6.8.

4-Dimethylaminobenzyl-1-and 2-cyclopentadiene (5b). The procedure above was followed using LAH (0.76 g, 20 mmol) and **3b** (2.01 g, 10.2 mmol) in diethyl ether (100 mL). Workup and purification as before (silica gel, 30:70 diethyl ether: hexanes) afforded **5b** as a pale yellow oil (1.54 g, 76%), and as an inseparable mixture of isomers in the ratio of 1:1 (by nmr). IR (thin film) 2885, 1613, 1519, 1475, 1443, 1340, 1161, 804 cm^{-1}; ^1H NMR (300 MHz, $CDCl_3$) δ 2.84 (m, 2 H, CHC*H*$_2$CH, isomer A or B), δ 2.89 (s, 3 H, N(C*H*$_3$)$_2$, isomer A or B), 2.89 (s, 3 H, N(C*H*$_3$)$_2$, isomer A or B), 2.95 (m, 2 H, CHC*H*$_2$CH isomer A or B), 3.60 (s, 2 H, Ph-C*H*$_2$, isomer A or B), 3.63 (s, 2 H, Ph-C*H*$_2$ isomer A or B), 5.98 (m, 1 H, *CH*, isomer A or B), 6.23 (m, 1 H, *CH*, isomer A or B), 6.39 (m, 1 H, *CH*, isomer A or B), 6.40 (m, 3 H, *CH*, isomer A and B), 6.68 (d, $J = 8.6$ Hz, 2 H, C*H*C(NMe$_2$)C*H*, isomer A or B), 6.69 (d, $J = 8.6$ Hz, 2 H, C*H*C(NMe$_2$)C*H*, isomer A or B) 7.04 (d, $J = 7.0$ Hz, 2 H, C*H*C(CH=Cp)C*H*, isomer A or B), 7.07 (d, $J = 7.0$ Hz, 2 H, C*H*C(CH=Cp)C*H*, isomer A or B). ^{13}C NMR (100.5 MHz, $CDCl_3$): δ 35.3 (C-6, isomer A or B), 36.3 (C-6 isomer A or B), 40.8 (N(*C*H$_3$)$_2$ isomer A and B), 41.2 (C-5, isomer A or B), 43.0 (C-5, isomer A or B), 112.90 (C-9, isomer A or B), 112.92 (C-9, isomer A or B), 126.9 (C-4, isomer A or B), 127.4 (C-4, isomer A or B), 128.3 (C-1, isomer A or B), 129.2 (C-2, isomer A or B), 129.2 (C-8, isomer A or B), 129.3 (C-8, isomer A or B), 131.1 (C-1, isomer A or B), 132.3 (C-3, isomer A or B), 133.7 (C-2, isomer A or B), 134.7 (C-3, isomer A or B), 146.6 (C-10, isomer A and B), 149.1 (C-7, isomer A and B). Anal. Calcd for $C_{14}H_{17}N$: C, 84.4; H, 8.5; N, 7.0. Observed: C, 84.7; H, 8.8; N, 6.9.

1-Iodo-8-(4-benzyloxybenzylcyclopentadienyl)naphthalene (6a). To a solution of **5a** (1.31 g, 5.0 mmol) in THF (15 mL) at 0 °C was added *n*-butyllithium (2.0 mL, 5.0 mmol, 2.5 M solution in hexanes), and the mixture was stirred for 1 h. Zinc chloride (0.82 g, 6.0 mmol) was added as a solution in THF (12 mL), and the mixture was stirred for a further 1 h. 1,8-Diiodonaphthalene (1.14 g, 3.0 mmol) in THF (5.0 mL) was introduced by syringe, and copper iodide (10 mg) was added in one portion. The reaction was stirred for 1 h and then poured into a separating funnel containing a saturated aqueous NH_4Cl solution (30 mL). The mixture was extracted into diethyl ether (3 × 50 mL), and the organic portions were

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(7) So, J.-H.; Boudjouk, P. *Inorg. Chem.* **1990**, *29*, 1592.

(8) Kauffman, G. B.; Albers, R. A.; Harlan, F. L. In *Inorganic Syntheses*; Parry, R., Ed.; McGraw-Hill Co.: New York, 1970; Vol. 12, pp 251−256.

(9) Watt, G. W. In *Inorganic Syntheses*; Audrieth, L. F., Ed.; McGraw-Hill: New York, 1950; Vol. 3, pp 194−196.

(10) *Organometallic Syntheses*, King, R. B., Ed.; Academic Press: New York, 1965; Vol. 1, p 72.

(11) Kohler, R. H.; Doll, K. H.; Fladerer, E.; Geike, W. A. *Transition Metal Chem.* **1981**, *6*, 126.

(12) House, H. O.; Koepsel, D. G.; Campbell, W. *J. Org. Chem.* **1972**, *37*, 1003.

(13) Stone, K. J.; Little, R. D. *J. Org. Chem.* **1984**, *49*, 1849−1853.

(14) Hafner, K. *Liebigs Ann. Chem.* **1957**, *606*, 79−89.

combined and dried over $MgSO_4$. The solvent was removed in vacuo, and the residue was purified by flash chromatography on silica gel (5:95 diethyl ether/hexanes) to afforded **6a** as a very pale yellow oil (0.831 g, 54%) and as two inseparable isomers (3- and 4-benzyloxybenzyl-substituted Cp) in the ratio 3:4 (by NMR). IR (solution in CH_2Cl_2): 2931, 1603, 1500, 1452, 196, 1176, 1023, 819 cm^{-1}. ^{1}H NMR (400 MHz, $CDCl_3$): δ 3.05−3.20 (m, 2 H, CHCH_2CH, minor isomer), 3.30−3.50 (m, 2 H, CHCH_2CH major isomer), 3.70 (s, 2H, CpCH_2 major isomer), 3.79 (s, 2H, CpCH_2 minor isomer), 5.05 (s, 2H, OCH_2Ph, major isomer), 5.05 (s, 2H, OCH_2Ph, minor isomer), 6.19 (m, 2 H, *CH*, major and minor isomers), 6.24 (m, 2 H, *CH* major and minor isomers), 6.86 (m, 4H, Ar−*H*, major and minor isomers), 7.06 (m, 2H, H_6, major and minor isomers), 7.20 (d, J = 8.0 Hz, 4H, Ar−*H*, major and minor isomers), 7.30−7.46 (m, 14 H, Ar−*H*, $H_{2,6}$ major and minor isomers), 7.74 (m, 2 H, H_3, major and minor isomers), 7.83 (m, 2 H, H_5, major and minor isomers), 8.19 (m, 2 H, H_7, major and minor isomers. A second compound **12a**, the product resulting from double cyclopentadienylation of diiodonaphthalene followed by intramolecular Diels Alder cyclization, was recovered from this reaction. This was obtained as a white crystaline solid (10%). IR (KBr): 3033, 2926, 1610, 1509, 1454, 1382, 1299, 1240, 1175, 1026, 819, 780, 736, 696 cm $^{-1}$. ^{1}H NMR (400 MHz, $CDCl_3$): δ 2.12 (bd, J = 18.7 Hz, 1 H, dicyclopentadiene-$H_{1,exo}$), 2.79 (m, 1H, dicyclopentadiene−H_7), 2.81 (m, 1 H, dicyclopentadiene−H_{3a}), 3.06(d, J = 15.5 Hz, CH_2Ph), 3.08 (bs, 1H, dicyclopentadiene−H_4), 3.10 (bd, J = 18.7 Hz, 1H, dicyclopentadiene−$H_{1,endo}$), 3.32 (bs, 1H, dicyclopentadiene−H_8), 3.34 (d, J = 15.5 Hz, 1H, CH_2Ph), 3.42 (d, J = 16.0 Hz 1 H, CH_2Ph), 3.56(d, J = 16.0 Hz, 1 H, CH_2Ph), 5.08 (s, 2 H, OCH_2Ph), 5.17 (bs, 1 H, dicyclopentadiene−H_2), 5.77 (bs, 1 H, dicyclopentadiene−H_6), 6.83 (d, J = 8.3 Hz, 2 H, Ar−*H*), 6.97 (d, J = 8.3 Hz, 2 H, Ar−H), 7.02 (d, J = 8.3 Hz, 2 H, Ar−H), 7.18 (m, 3 H, Ar−*H*), 7.3−7.42 (m, 10 H, Ar−*H*), 7.47 (m, 2 H, Ar−*H*), 7.60 (dd, J = 1.7, 7.5 Hz, 1 H, Ar−*H*), 7.67 (d, J = 7.5 Hz, 1 H, Ar−*H*). ^{13}C NMR (100.5 MHz, $CDCl_3$): δ 34.5, 36.9, 37.8, 54.7, 54.9, 56.3, 65.0, 67.8, 70.2, 70.3, 114.8, 115.0, 117.8, 124.3, 125.1, 125.5, 125.8, 126.7, 127.1, 127.7, 127.74, 128.1, 128.14, 128.8, 128.7, 128.8, 130.1, 130.4, 130.8, 131.8, 132.0, 133.9, 137.3, 137.4, 138.8, 142.1, 146.1, 153.0, 157.3, 157.5. Anal. Calcd for $C_{48}H_{40}O_2$: C, 88.9; H, 6.2. Observed: C, 88.7; H, 6.2.

This Diels−Alder product (**12a**), together with an isomer **13a**, was also obtained from diiodonaphthalene by treatment with excess **5a** anion as follows. Compound **5a** (0.79 g. 3.0 mmol) was dissolved in THF (10 mL) and cooled to 0 °C. BuLi (01.2 mL, 3.0 mmol, 2.5 M solution in hexanes) was added dropwise, and the reaction was stirred for 1 h, before zinc chloride (0.68 g, 5.0 mmol) in THF (5 mL) was added. After a further 1 h, 1,8-diiodonaphthalene (0.30 g, 0.79 mmol) and CuI (0.03 g, 0.15 mmol) were added in THF (15 mL). The mixture was stirred at room temperature for 2 h, after which it had become black. The solution was poured into a separating funnel charged with concentrated aqueous NH_4Cl solution (30 mL) and was extracted with diethyl ether (2 × 30 mL). The combined organic extracts were washed with water (2 × 50 mL) and dried over $MgSO_4$. The Diels−Alder products were obtained as an inseparable mixture of isomers in the ratio 1:2 (by NMR analysis of the crude material) and in 72% yield after purifcation by column chromatography on silica gel with 30:70 ether/hexanes as the eluant. A portion of the mixture was dissolved in a minimum of hot hexane and allowed to stand overnight. Colorless crystals were obtained, which were shown to be the major isomer **12a** by comparison with the NMR spectrum of the product obtained above. After evaporation, the mother liquor was found to be greatly enriched in the minor isomer **13a**. ^{1}H NMR (400 MHz, $CDCl_3$) δ 2.11 (bd, J = 18.7 Hz, 1H, $H_{1\alpha}$), 2.79 (bs, 1 H, H_{3a}) 2.80 (bs, 1 H, H_7), 2.95 (m, 2 H, H_4, H_8), 3.08 (m, 2 H, $H_{1\beta}$, CH_2Ph), 3.31 (bs, 1 H, CH_2Ph) 3.44 (m, 2 H, CH_2Ph), 5.05 (s, 2 H, OCH_2Ph), 5.08 (s, 2 H, OCH_2Ph), 5.06 (bs, 1 H, H_2), 5.68 (bs, 1 H, H_5), 6.82 (d, J = 8.3 Hz, 2 H, Ar−*H*), 6.92 (d, J = 8.3 Hz, 2 H, Ar−*H*), 6.96 (d, J = 8.3 Hz, 2 H, Ar−*H*), 7.14 (m, 3 H, $H_{5'}$, Ar−*H*), 7.30−7.45 (m, 10 H, $H_{3',4',6'}$, Ar−*H*), 7.60 (dd, J = 1.7, 7.5 Hz, 1 H, $H_{2'}$, Ar−*H*), 7.67 (d, J = 7.5 Hz, 1 H, $H_{7'}$, Ar−*H*).

1-Iodo-8-(4-dimethylaminobenzylcyclopentadienyl)-naphthalene (6b). The same procedure as for the preparation of **6a** was followed. Cyclopentadiene **5b** (1.55 g, 7.8 mmol) in dry THF (15 mL) was treated with *n*-butyllithium (3.75 mL, 6.0 mmol, 2.5 M solution in hexanes) at 0 °C followed by zinc chloride (1.63 g, 12.0 mmol). The mixture was stirred for 1 h, and 1,8-diiodonaphthalene (1.895 g, 5.0 mmol) in THF (1.0 mL) was added along with copper iodide (2 mg). The mixture was stirred for a further 1 h and worked up and purified as above to afford **6b** as a pale yellow oil (0.95 g, 42%) as two inseparable isomers (3- and 4-dimethylaminobenzyl-substituted Cp) in the ratio 3:4 (by NMR). IR (solution in CH_2Cl_2): 2926, 2853, 1613, 1558, 1520, 456, 1358, 819 cm^{-1}. Major Isomer ^{1}H NMR (300 MHz, $CDCl_3$): δ 2.88 (s, 6 H, N(CH_3)$_2$, major isomer), 2.89 (s, 6 H, N(CH_3)$_2$), 2.89 (m, 4 H, CH_2 (Cp) major and minor isomers), 3.64 (s, 2 H, CpCH_2Ph, major isomer), 3.71 (s, 2 H, CpCH_2Ph, minor isomer), 6.15 (m, 2 H, Cp−*H*, major and minor isomers), 6.26 (m, 2 H, Cp−*H*, major and minor isomers), 6.66 (d, J = 8.9 Hz, 2 H, Ar−*H*, major isomer), 6.68 (d, J = 8.9 Hz, 2 H, Ar−*H*, minor isomer), 7.02 (dd, J = 7.4, 7.6 Hz, 1 H, H_6, major isomer), 7.04 (dd, J = 7.4, 7.6 Hz, 1 H, H_6, minor isomer), 7.12 (d, J = 8.9 Hz, 4 H, Ar−*H*, major and minor isomers), 7.37 (m, 4 H, $H_{2,4}$, major and minor isomers), 7.70 (dd, J = 3.4, 6.8 Hz, 1 H, H_3, major isomer), 7.74 (dd, J = 3.4, 6.8 Hz, 1 H, H_3, minor isomer), 7.78 (bd, J = 7.9 Hz, H_5, minor isomer), 7.80 (bd, J = 7.9 Hz, H_5, major isomer), 8.14 (dd, J = 1.3, 7.3 Hz, H_7, minor isomer), 8.16 (dd, J = 1.3, 7.3 Hz, H_7, major isomer). Anal. Calcd for $C_{24}H_{22}NI$: C, 63.9; H, 4.9. Observed: C, 63.9; H, 4.8.

As before, a second product is formed in this reaction through double cyclopentadienylation of diiodonaphthalene. The resulting dicyclopentadiene product was recovered from the reaction mixture in 16% yield as a white crystaline solid (0.418 g, 0.8 mmol). Mp: 208−210 °C. IR (KBr): 2900, 1616, 1521, 1443, 1350, 1225, 1159, 948, 816, 804, 881, 774 cm $^{-1}$. ^{1}H NMR (400 MHz, $CDCl_3$): δ 2.11 (bd, J = 18.7 Hz, 1 H, dicyclopentadiene−H_{1exo}), 2.78 (bs, 1 H, dicyclopentadiene−H_7), 2.82 (bs, 1 H, dicyclopentadiene−H_{3a}), 2.87 (s, 6 H, *NMe*$_2$), 2.96 (s, 6 H, N*Me*$_2$), 2.98 (d, J = 15.9 Hz, 1 H, CH_2Ph), 3.05 (bd, J = 18.7 Hz, 1H, dicyclopentadiene−$H_{1,endo}$), 3.06 (bs, 1 H, dicyclopentadiene−H_4), 3.31 (d, J = 15.9 Hz, 2 H, CH_2Ph), 3.32 (bs, 1 H, dicyclopentadiene−H_8), 3.39 (d, J = 14.7 Hz, 2 H, CH_2Ph), 3.56 (d, J = 16.5 Hz, 2 H, CH_2Ph) 5.16 (s, 1 H, dicyclopentadiene−H_2) 5.78 (s, 1 H, dicyclopentadiene−H_6), 6.62 (d, J = 8.6 Hz, 2 H, Ar−*H*), 6.76 (d, J = 8.6 Hz, 2 H, Ar−*H*), 6.99 (d, J = 8.6 Hz, 2 H, Ar−*H*), 7.16 (m, 3 H, C-5, Ar−*H*), 7.35 (m, 3 H, Ar−H), 7.59 (dd, J = 1.8, 6.7 Hz, 1 H, Ar−H), 7.65 (d, J = 7.9 Hz, 1 H, Ar−H). ^{13}C NMR (100.5 MHz, $CDCl_3$): δ 34.6, 36.7, 37.7, 41.1, 41.2, 54.89, 54.94, 56.4, 65.1, 67.9, 113.1, 113.2, 117.9, 124.3, 125.1, 125.5, 125.8, 126.7, 126.8, 127.8, 127.9, 128.2, 129.8, 130.1, 131.0, 134.0, 139.1, 142.6, 146.4, 149.3, 149.4, 153.2. Anal. Calcd for $C_{38}H_{38}N_2$: C, 87.4; H, 7.3; N, 5.4. Found: C, 87.1; H, 7.3; N, 5.2. The structure of this compound **(12b)** has been established by X-ray analysis.

The Diels−Alder products **12b** and **13b** were obtained separately by treatment of **5b** (0.40 g, 2.0 mmol), dissolved in THF (10 mL) at 0 °C with BuLi (0.80 mL, 2.0 mmol, 2.5 M solution in hexanes). The solution was stirred for 1 h, before zinc chloride (0.41 g, 3.0 mmol) in 5 mL of THF was added. After a further 1 h 1,8-diiodonaphthalene (0.15 g, 0.4 mmol) and CuI (0.02 g, 0.1 mmol) were added in 10 mL of THF. The reaction was worked up as in the preparation of **12**,**13a**, and **12b** was isolated from the mixture by crystallization. After evaporation, the mother liquor was found to be greatly enriched in the minor isomer **13b**. ^{1}H NMR (400 MHz, $CDCl_3$): δ 2.10 (bd, J = 20.0 Hz, 1 H, C-1−Hα), 2.72 (bs, 1 H,

Table 1. Data for the X-ray Diffraction Study of 12b

chemical formula	**12b**, $C_{38}H_{38}N_2$
a, Å	10.1514(13)
b, Å	12.533(2)
c, Å	23.520(2)
β, deg	101.15(1)
V, Å^3	2935.9
Z	4
fw	522.74
space group	$P2_1/n$ [C^5_{2h}; No. 14]
T, °C	21(1)
λ, Å	1.54178, graphite monochromator
ρ_{calc}, g cm^{-3}	1.183
μ, mm^{-1}	0.484
absorp corr	empirical transm factors 0.939−1.00
data collection	$\pm h, -k, -l$ (to $2\theta = 156°$)
no. of reflns measd	6314; 6165 in unique set; $R_{int} = 0.012$
R^a	0.0403
$R_w{}^b$	0.0524

[a] $R = \sum||F_o| - |F_c||/\sum|F_o|$. [b] $R_w = \{\sum w[|F_o| - |F_c|]^2/\sum w|F_o|^2\}^{1/2}$.

C-7), 2.73 (bs, 1 H, C-3a), 2.87 (bs, 1 H, C8), 2.88 (bs, 1 H, CH_2Ph), 2.90 (d, $J = 8.0$ Hz, C-4), 3.00 (bd, $J = 20.0$ Hz, 1H, C-1−Hβ), 3.26 (d, $J = 17.6$ Hz, 1 H, CH_2Ph), 3.32 (bs, 1 H, CH_2Ph), 3.49 (d, $J = 17.6$ Hz, 1 H, CH_2Ph), 5.06 (s, 1 H, C-2), 5.68 (s, 1 H, C-5), 6.60 (d, $J = 8.6$ Hz, 2 H, Ar−H), 6.92 (d, $J = 8.6$ Hz, 2 H, Ar−H), 7.08 (d, $J = 8.6$ Hz, 2 H, Ar−H), 7.16 (m, 1 H, C-5′), 7.35 (m, 3 H, C-3′, C-4′, C-6′), 7.59 (dd, $J = 1.8$, 6.7 Hz, 1 H, C-2′), 7.65 (d, $J = 7.9$ Hz, 1 H, C-7′).

X-ray Structure Determination of $C_{38}H_{38}N_2$ (12b). Crystallographic data for compound **12b** are summarized in Table 1. Data were collected on a Nonius CAD-4U diffractometer (Cu Kα radiation, $\lambda = 1.54178$ Å).[15] Data were processed using the Nonius MolEN package;[16] the structure was solved by direct methods (SIR-92).[17] Full-matrix least-squares refinement was carried out using the Oxford University CRYSTALS-PC system.[18] All nonhydrogen atoms were refined using anisotropic displacement parameters; H atoms were refined using isotropic displacement parameters. Drawings were produced using the Oxford University program CAMERON.[19] Bond lengths and angles lie within expected ranges for strained molecules. A full report on the structure is available as a CIF file.

3,3′-Bis(4-benzyloxybenzyl)-1,1′-bis(8-iodo-1-naphthyl)ferrocene (7a). To a solution of **5a** (0.50 g, 0.97 mmol) in dry THF (10 mL) at −78 °C was added KO^{t}Bu (0.11 g, 1.0 mmol) also in THF (2 mL), and the dark red mixture was stirred for 15 min. $FePy_4(SCN)_2$ (0.98 g, 2.0 mmol) (previously washed with dry THF (3 × 10 mL)) was added as a slurry in one portion before the flask was allowed to warm slowly to room temperature. After stirring for a further 1 h the reaction was quenched with water and extracted with diethyl ether (3 × 50 mL). The combined organic phases were washed with saturated aqueous $CuSO_4$ (4 × 50 mL) and water (50 mL). Purification by flash chromatography on silica gel (30:65:5 toluene/hexanes/ether) afforded **7a** as a red solid (0.329 g, 63%) and as a 1:1 mixture of *dl* and *meso* forms. IR (KBr): 3031, 2910, 1610, 1509, 1452, 1239, 1174, 1026, 816, 763, 735, 696 cm^{-1}. ^{1}H NMR (400 MHz, $CDCl_3$): δ 3.58 (s, 2 H, FcCH_2), 3.67 (s, 2 H, FcCH_2), 4.05, 4.15, 4.19, 4.20, 4.27, 4.43 (2 pairs of 3 multiplets, 6 H, α and β Fc−H, *dl* and *meso*), 4.99 (s, 4 H, OCH_2Ph, *dl* and *meso*), 6.83 (d, $J = 8.25$ Hz, 4H, Ar−H, *dl* and *meso*), 6.98 (dd, $J = 7.33$, 7.33 Hz, 0.5 H, H_6 *dl* or *meso*), 6.99 (dd, $J = 7.33$, 7.33 Hz, 1 H, H_6 *dl* or *meso*), 6.99 (dd, $J = 7.6$, 7.6 Hz, 1 H, H_3 *dl* or *meso*), 7.06 (dd, $J = 7.6$, 7.6 Hz, 1 H, H_3 *dl* or *meso*), 7.11 (d, $J = 8.9$ Hz, 2H, Ar−H, *dl* or *meso*), 7.14 (d, $J = 8.9$ Hz, 2H, Ar−H, *dl* or *meso*), 7.24 (m, 1 H, Ar−H, *dl* or *meso*), 7.22−7.42 (m, 11 H, Ar−H), 7.55 (dd, $J = 9.2$, 0.9 Hz, H_4, *dl* or *meso*), 7.57 (dd, $J = 9.2$, 0.9 Hz, H_4, *dl* or *meso*), 7.77 (dd, $J = 8.3$, 1.5 Hz, H_5, *dl* or *meso*), 7.78 (dd, $J = 8.3$, 1.5 Hz, H_5, *dl* or *meso*), 8.05 (dd, $J = 7.0$, 1.22 Hz, H_2, *dl* or *meso*), 8.06 (dd, $J = 7.3$, 1.2 Hz, H_7, *dl* or *meso*), 8.12 (dd, $J = 7.3$, 1.2 Hz, H_7 *dl* or *meso*). Anal. Calcd for $C_{58}H_{44}FeO_2I_2$: C, 64.3; H, 4.1. Observed: C, 64.0; H, 3.7.

3,3′-Bis(4-dimethylaminobenzyl)-1,1′-bis(8-iodo-1-naphthyl)ferrocene (7b). Following the same procedure as above, the anion of **6b** (0.70 g, 1.55 mmol) was formed in THF (10 mL) at −78 °C with KO^{t}Bu (0.20 g, 1.8 mmol). Freshly washed (3 × 10 mL) $FePy_4(SCN)_2$ (0.98 g, 2.0 mmol) was added, and the reaction was allowed to warm to room temperature followed by stirring for 1 h. Workup and purification as above afforded **7b** (0.45 g, 61%) as a red solid and as a 1:1 mixture of *dl* and *meso* forms. A small amount of **6b** (0.118 g, 17%) was also recovered after chromatography. IR (KBr): 2882, 1612, 1520, 1350, 1192, 1162, 947, 81, 763 cm^{-1}. ^{1}H NMR (400 MHz, $CDCl_3$): δ 2.87 (s, 6 H, *dl* or *meso*), 2. 88 (s, 6 H, *dl* or *meso*), 3.59 (s, 4 H, *dl* or *meso*), 3.67 (s, 4 H, *dl* or *meso*), 4.07, 4.17, 4.19, 4.21, 4.22, 4.40 (2 pairs of 3 multiplets, 12 H, α and β Fc−H, *dl* and *meso*), 6.62 (d, $J = 6.1$ Hz, 4 H, Ar−H, *dl* or *meso*), 6.64 (d, $J = 6.1$ Hz, 4 H, Ar−H, *dl* or *meso*), 6.9 (m, 6 H, H_3 *dl* and *meso,* H_5, *dl* or *meso*), 7.03 (dd, $J = 7.6$, 7.64 Hz, 2 H, H_5, *dl* or *meso*), 7.11 (m, 4 H, Ar−H, *dl* and *meso*), 7.54 (d, $J = 7.9$ Hz, 2 H, H_4, *dl* or *meso*), 7.56 (d, $J = 7.9$ Hz, 2 H, H_4, *dl* or *meso*), 7.78 (d, $J = 8.3$ Hz, 4 H, H_5, *dl* and *meso*), 8.04 (dd, $J = 0.9$, 7.3 Hz, 2 H, H_5, *dl* or *meso*), 8.06 (dd, $J = 0.9$, 7.0 Hz, 4 H, H_7, *dl* and *meso*), 8.09 (dd, $J = 0.9$, 7.3 Hz, 2 H, H_5, *dl* or *meso*). Anal. Calcd for $C_{48}H_{42}FeN_2I_2$: C, 60.2; H, 4.4; N, 2.9. Observed: C, 59.7; H, 4.6; N, 2.8.

3,3′-Bis(4-benzyloxybenzyl])-1,1′-bis(8-cyclopentadienyl-1-naphthyl)ferrocene (8a). Cyclopentadienylzinc chloride was prepared from freshly cracked cyclopentadiene (132 mg, 2.0 mmol) in dry THF (30 mL) at 0 °C by the addition of *n*-butyllithium (0.8 mL, 2.0 mmol of a 2.5 M solution in hexanes) followed by zinc chloride (54 mg, 4.0 mmol) in THF (10 mL). The mixture was stirred for 1 h, and **7a** (328 mg, 0.3 mmol) in THF (5 mL) was introduced by syringe. Copper iodide (3 mg, 1.5 × 10^5 mol, 5 mol %) was added, and the reaction mixture was allowed to warm to room temperature. After stirring for 30 min the solution had become very dark brown. The mixture was poured into a separating funnel charged with a saturated aqueous solution of NH_4Cl (25 mL) and extracted with diethyl ether (3 × 50 mL). The organic portions were combined and washed with water (2 × 50 mL) and brine (50 mL) before being dried over $MgSO_4$. The solvent was removed in vacuo, and purification by flash chromatography on silica gel (30:65:5 toluene/hexanes/ether) afforded **8a** (0.303 g, 98%), a complex mixture of diastereoisomers, as a red solid. ^{1}H NMR (400 MHz, $CDCl_3$): δ 2.1−2.5 (m, 2 H, CH_2 (Cp)), 2.60−2.90 (m, 2 H, CH_2 (Cp)), 3.30−3.95 (m, 10 H, Fc−CH_2, α and β Fc−H), 5.1 (bs, 4 H, OCH_2Ph), 5.74−6.05 (m, 6 H, CH (Cp), 6.67−7.04 (m, 10 H, Ar−H), 7.10−7.78 (m, 20 H, Ar−H). Anal. Calcd for $C_{68}H_{54}FeO_2$: C, 85.2; H, 5.6. Observed: C, 85.2; H, 5.7.

3,3′-Bis(4-dimethylaminobenzyl])-1,1′-bis(8-cyclopentadienyl-1-naphthyl)ferrocene (8b). Following the procedure as above, **7b** (0.520 g, 0.544 mmol) and copper iodide (10 mg) were added to a solution of cyclopentadienylzinc chloride (15.0 mmol in THF (20 mL)) at 0 °C. After warming to room temperature and stirring for 30 min the mixture was worked up and purified as above to afford **8b** (0.392 mg, 86%) as a complex mixture of diastereoisomers, as a red solid. ^{1}H NMR (400 MHz, $CDCl_3$): δ 2.30−2.54 (m, 2 H, CH_2 (Cp)), 2.60−2.80

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(15) Straver, L. H. *CAD4-EXPRESS*; Enraf-Nonius: Delft, The Netherlands, 1992.

(16) Fair, C. K. *MolEN, An Interactive Structure Solution Procedure*; Enraf-Nonius: Delft, The Netherlands, 1990.

(17) Altomare, A.; Cascarano, G.; Giacovazzo G.; Guagliardi A.; Burla M. C.; Polidori, G.; Camalli, M. *J. Appl. Crystallogr.* **1994**, *27*, 435.

(18) Watkin, D. J.; Prout, C. K.; Carruthers, J. R.; Betteridge, P. W. *CRYSTALS Issue 10*; Chemical Crystallography Laboratory: University of Oxford, Oxford, 1996.

(19) Watkin, D. J.; Prout, C. K.; Pearce, L. J. *CAMERON*; Chemical Crystallography Laboratory: University of Oxford, Oxford, 1996.

Table 2. Ferrocene Polymers

experiment	monomer (mg)	reaction conditions	M_w (DP$_w$)[d]	M_n	polymer (mg)[e]
1	**8a** (65)	*a*	188 500 (186)	18 800	**1d** (60)
2	**8a** (80)	*b*	49 300 (49)	13 500	**1d** (61)
3	**8b** (50)	*c*	14 100 (16)	2700	**1e** (49)

[a] THF, $(Me_3Si)_2NK$, $FePy_4(SCN)_2$, [8] 55 °C, 10 days. [b] 1,2-Dimethoxyethane, $(Me_3Si)_2Na$, $FeCl_2$, 100 °C, 2 days. [c] THF/toluene (1:1), *n*-C_4H_9Li, $FePy_4(SCN)_2$,[8] reflux, 2 days. [d] Weight average degree of polymerization. [e] After processing to remove monomer and metal salts (see Experimental Section).

Table 3. Ferrocene-Nickelocene Copolymers

experiment	monomer (mg)	reaction conditions	M_w (DP$_w$)[d]	M_n	polymer (mg)[e]
1	**8a** (65)	*a*	7900 (8)	1700	**1f** (30)
2	**8b** (100)	*b*	43 700 (49)	4100	**1g** (95)
3	**9a** (350)	*c*	26 300 (19)	8400	**1h** (56)[f]

[a] Pyridine, $(Me_3Si)_2NK$, $Ni(NH_3)_6Br_2$, [9] 100 °C, 7 days. [b] Pyridine, $(Me_3Si)_2NNa$, $NiBr_2$ 1,2-dimethoxyethane, 100 °C, 7 days. [c] THF, $(Me_3Si)_2NNa$, $NiPy_4(SCN)_2$,[8] 25 °C, 3 days. [d] Weight average degree of polymerization. [e] After processing to remove monomer and metal salts. See Experimental Section. [f] Unreacted starting material (250 mg) was recovered.

(m, 2 H, CH_2 (Cp)), 2.88, 2.89, 2.92 (bs 12 H, N(CH_3)$_2$) 3.12−3.96 (m, 12 H, Fc−CH_2, α and β Fc−H), 5.76−6.12 (m, 6 H, C*H*, (Cp)), 6.59−7.76 (m, 20 H, Ar−H). Anal. Calcd for $C_{58}H_{52}FeN_2$: C, 83.7; H, 6.3; N, 3.4. Observed: C, 83.5; H, 6.6; N, 3.1.

3,3′-Bis(4-benzyloxybenzyl)-1,1′-bis(8-[4-benzyloxybenzylcyclopentadienyl]-1-naphthyl)ferrocene (9a). Following the procedure above, **7a** (0.30 g, 0.28 mmol) was added in THF (1 mL) to a solution of 4-benzyloxybenzylcyclopentadienylzinc chloride prepared from **4a** (0.42 g, 1.6 mmol), *n*-butyllithium (0.6 mL, 1.5 mmol, 2.5 M solution in hexanes), and zinc chloride (0.41 g, 3.0 mmol) as before, in THF (10 mL). Copper iodide (10 mg) was added, and the solution was stirred at room temperature for 1 h, after which it had become very dark in color. Workup and purification (silica gel, 50:40:10 toluene/hexanes/ether) afforded **9a** (complex mixture of isomers) as a red solid (0.370 g, 99%). IR (KBr): 3031, 2900, 1610, 1510, 1454, 1376, 1298, 1239, 1174, 1025, 824, 771, 735, 696 cm^{-1}. ^{1}H NMR (400 MHz, $CDCl_3$): δ 2.60−2.80 (m, 4 H, CH_2 (Cp)), 3.20−4.00 (m, 16 H, CpCH_2, Fc−CH_2, α and β Fc−H), 4.99 (bs, 8 H, OCH_2Ph), 5.50−6.90 (m, 4 H, C*H*, (Cp)), 6.74−7.02 (m, 16 H, Ar−H), 7.16−7.44 (m, 28 H, Ar−H), 7.59 (m, 2 H, H_2 or H_7), 7.70 (m, 2 H, H_2 or H_7). Anal. Calcd for $C_{96}H_{78}FeO_4$: C, 85.3; H, 5.8. Observed: C, 85.1; H, 5.8.

General Procedure for Preparation of Ferrocene Polymers. The monomer (1 equiv) was dissolved in the solvent of choice (5 mL approximately) under argon, and 1.2 equiv of base was added at room temperature. The mixture generally became much darker in color, and after stirring for 30 min the appropriate metal salt was introduced (1 equiv) either as a slurry ($FePy_4(SCN)_2$) in the solvent used or as a solid ($FeCl_2$) in one portion. The mixture was heated to the temperature specified and stirred for the time given (see Tables 1 and 2). After 2 or 3 days additional equivalents of base and metal salt were generally added.

The reaction was stopped when it was judged that the polymerization was complete, as evidenced by the amount of precipitation and color of the supernatant (usually clear and fairly colorless). The mixture was cooled and the solvent was removed under reduced pressure. The solid was washed with ether (2 × 10 mL) by stirring for 15 min followed by filtration. The residue was further washed with methanol or ethanol (10 mL), water (10 mL), and HCL (1 N, 10 mL) in an analogous manner. This was followed by rinsing with ethanol and ether to dry the sample before storing under vacuum for several hours. The remaining solid was continuously extracted overnight in a Soxhlet apparatus with pyridine as the solvent. After removal of solvent the solid was further washed with cold then hot toluene, to remove lower mass components, before determination of molecular weights.

General Procedure for Preparation of Ferrocene−Nickelocene Copolymers. The scale of each polymerization reaction and the yield of polymer obtained are given in Tables 2 and 3. The monomer (1 equiv) was dissolved in pyridine (freshly distilled from CaH_2) (5 mL) under argon, and sodium bis(trimethylsilyl)amide (1.2 equiv) was added at room temperature. The mixture generally became much darker, and after stirring for 30 min the appropriate metal salt was introduced (1 equiv) as a solid in one portion. The mixture was heated to 100 °C and stirred for the time given. After 2 or 3 days extra equivalents of base and metal salt were added.

The reaction was deemed complete when there was a considerable amount of precipitation and the supernatant was fairly colorless. The mixture was cooled and solvent was removed under reduced pressure. The solid was washed with ether (2 × 10 mL) by stirring for 15 min followed by filtration. The residue was further washed with methanol or ethanol (10 mL) in an analogous manner, and this was followed by rinsing with ether and drying under vacuum. The solids were extracted with pyridine in a Soxhlet apparatus until the solution over the sample was clear. The solutions were evaporated to dryness, and the extracts were subjected to GPC analysis.

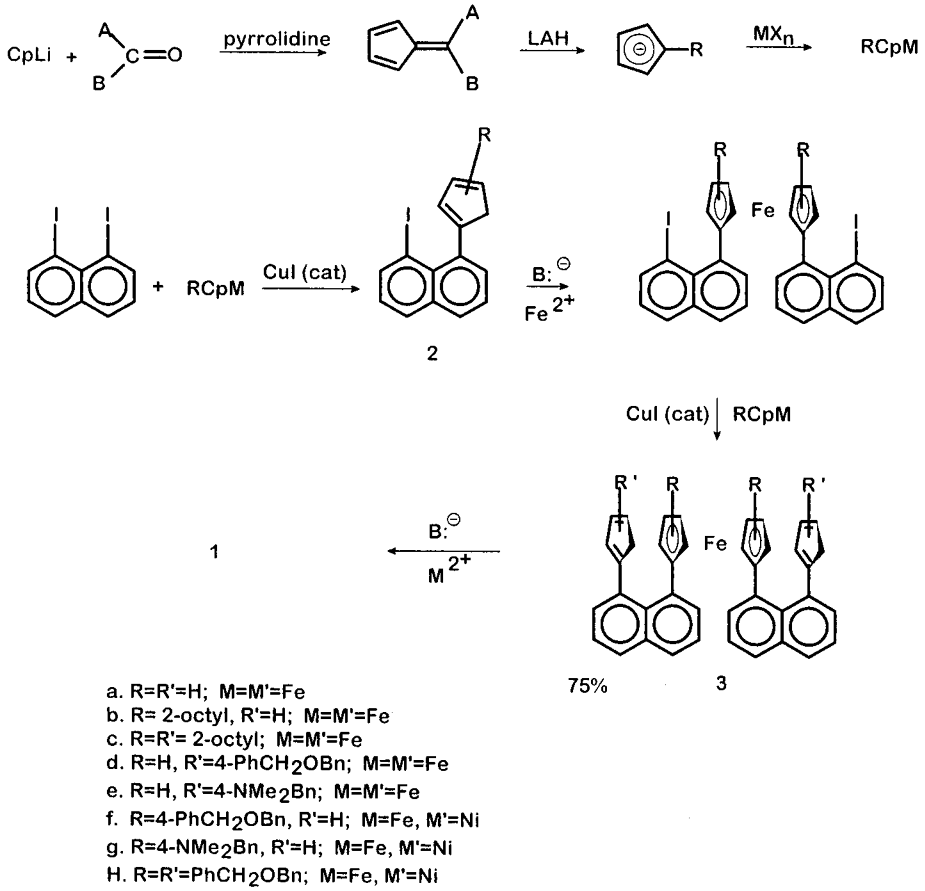
Results and Discussion

The general synthetic sequence for the preparation of monomers **3** and their conversion to polymers **1** is summarized in Scheme 1. This sequence employs readily available, inexpensive starting materials, is convergent, and is relatively short. Moreover, it is readily adapted to the preparation of wide variety of cyclopentadienyl-ring-substituted analogues of the parent monomer **3** (R = R′ = H), employing a flexible and operationally simple route. Finally, copolymers can be prepared in which ferrocene nuclei alternate with other metallocene centers along the polymer chain.

A significant improvement in the cyclopentadienyl coupling steps has now been achieved by replacement of $RCpCu{\cdot}SMe_2$ reagents with RCpZnCl salts. Use of the copper reagent required that the coupling reactions be carried out for extended periods of time at −23 °C, since the copper salts decompose rapidly above this temperature. With the more robust zinc salts, the reaction can be carried out conveniently at 0 °C with considerably improved yield and ease of workup. For example, intermediates **2** (R = H) and (R = 2-octyl) were obtained in 95% and 94% yields, respectively, using cyclopentadienylzinc salts, compared with 49% and 79% yields for these products obtained with the earlier protocol. Moreover, we found that the coupling reactions employing zinc salts are catalyzed by CuI and, under these conditions, are complete within an hour or less at 0 °C. Indeed, the coupling reaction becomes so facile under these reaction conditions that small amounts of the Diels−Alder cycloadducts, derived from the double cyclopentadienylation of diiodonaphthalene, are formed along with **2**.

Following the first preparation of polymeric, stacked ferrocenes, and ferrocene copolymers, a principal focus of our research has been the preparation of more soluble analogues of the parent polymers. We had earlier reported[4] that a modest improvement in the solubility of the parent polymer **1a** could be achieved by introduc-

Scheme 1



ing long chain aliphatic substituents on one or both of the cyclopentadienyl rings of the precursor monomer **3**. Such a general strategy has been employed in improving the solubility of poly(*p*-phenylene), polythiophenes, poly(*p*-arylenevinylene), poly(*p*-phenyleneethynylene), and polypyrroles[20] Thus, the benzene-soluble fraction of the parent unsubstituted polymer **1a,** obtained as a dark red solid, had only a modest M_w and M_n of 3000 (DP = 5) and 2300, respectively. By contrast, polymerization of monomer **3b**, in the presence of sodium hexamethyldisilazide and ferrous chloride, gave a polymer **1b**, from which a benzene-soluble, dark purple fraction, with M_w= 18 400 (DP = 25) and M_n = 14 400 was obtained. Nevertheless, much of the product polymer remained insoluble in common solvents. In an attempt to further improve polymer solubility, a doubly substituted monomer **3c** was prepared and subjected to polymerization. The product polymer was found to be insoluble in benzene, but slightly soluble in THF. GPC analysis of this solution showed a bimodal peak distribution with a major peak at 4700 and a minor component at 136 000.

These results prompted us to examine the use of cardo groups[21] to improve the solubility of these metallocene polymers. Such bulky substituents have been shown to improve the solubility of a number of polyimides, with little reduction in their thermal stability.[22] Accordingly, the fulvenes **4a** and **4b**, prepared in high yield from the readily available aldehydes,[13] were reduced, following the method of Hafner[14] to give **5a** and **5b** as a mixture of 3- and 4-substituted 1-arylcyclopentadienes. These were, in turn, coupled with 1,8-diiodonaphthalene to give a 3:4 mixture of the isomeric 1-iodo-8-(3 and 4-arylmethylcyclopentadienyl)naphthalenes **6a** and **6b** (Scheme 2).

It is of interest to note in passing that these products were each accompanied by small amounts of a mixture of two isomeric Diels–Alder products, derived through biscyclopentadienylation of the diiodide. These cycloaddition products are formed in approximately a 2:1 ratio either directly by biscyclopentadienylation of diiodonaphthalene or by cyclopentadienylation of **6a** or **6b**. An X-ray crystal structure analysis of the major isomer derived from **6b** (Figure 1) shows this material to have structure **12b**.

TOCSY NMR analysis[23] of the well-separated vinyl proton resonances in the bicycloheptene and cyclopentene rings in both the crystalline material **12b** and in

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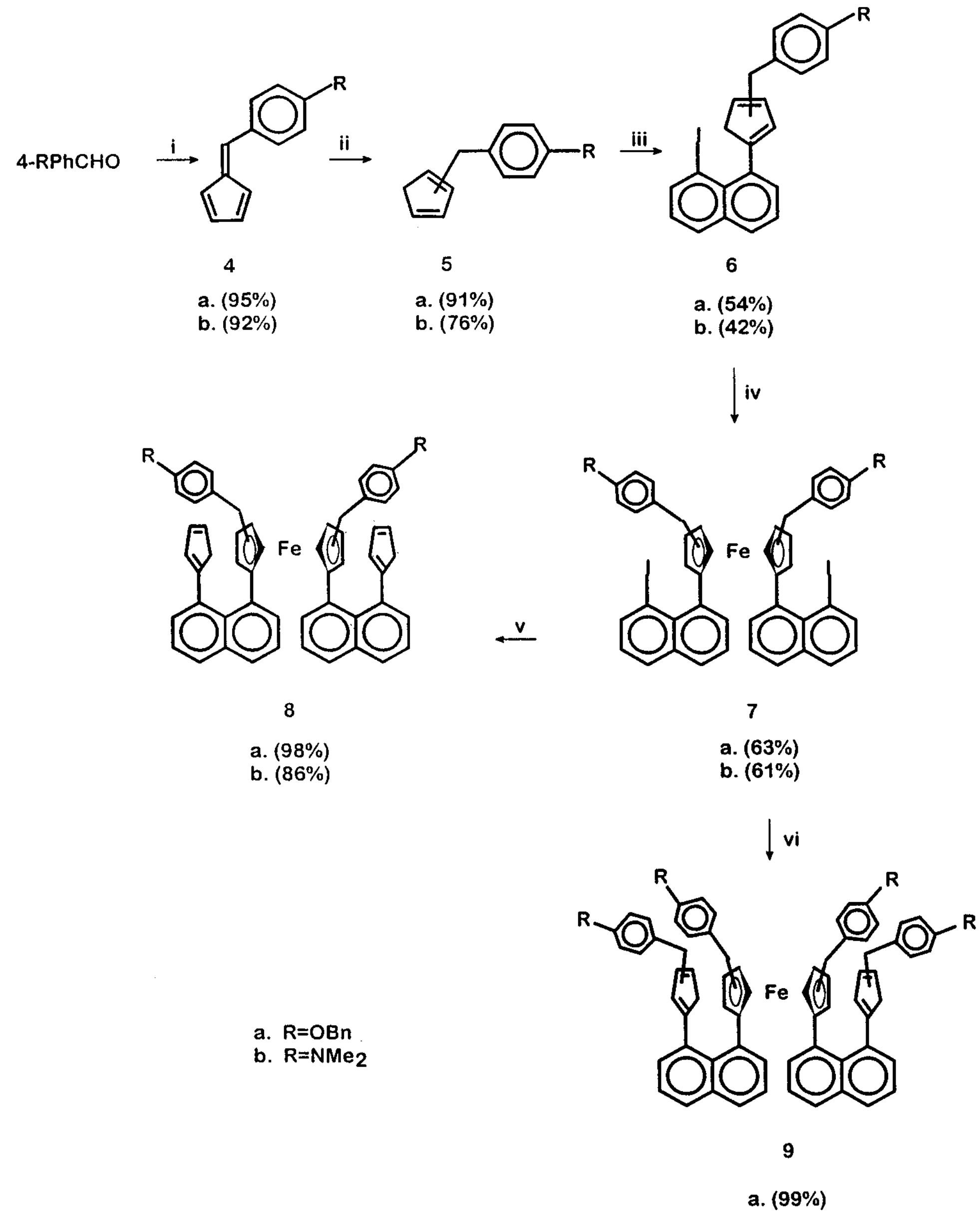
(20) Rehahn, M.; Schuter, A. D.; Lenz, R. W. *Eur. Polym. J.* **1983**, *19*, 1043. Jen, K. Y.; Oboodi, R.; Elsembaumer, R. L. *Polym. Mater. Sci. Eng.* **1985**, *53*, 79. Osterholm, J.-E.; Laakao, M. J.; Nyholm, P. *Synth. Met.* **1989**, *28*, C435. Askari, S. H.; Rughooputh, S. D.; Wudl, F. *Synth. Met.* **1989**, *29*, E129. Han, C.-C.; Elsembaumer, R. L. *Mol. Cryst. Liq. Cryst.* **1990**, *189*, 183. Giesa, R.; Schulz, R. C. *Makromol. Chem.* **1990**, *191*, 857. Ruhe, J.; Ezquerra, T. A.; Wegner, G. *Synth. Met.* **1989**, *28*, C177.

(21) Korshak, V. V.; Vinogradova, S. V.; Vygodskii, Y. S. *Rev. Macromol. Chem.* **1974**, *12*, 45–142.

(22) Yang, C.-P.; Lin, J.-H. *J. Polm. Sci., Part A: Polym. Chem.* **1993**, *31*, 2153-2163. Hsiao, S.-H.; Li, C.-T. *Macromolecules* **1998**, *31*, 7213–7127.

(23) TOCSY (total correlation spectroscopy). Levitt, M.; Freeman, R.; Frenkiel, T. *J. Magn. Reson.* **1982**, *47*, 328. Bax, A.; Davis, D. *J. Magn. Reson.* **1985**, *65*, 355. Experiments were carried out with an arrayed mix time from 0 to 0.20 s, with the best results being obtained with a mix of 0.15 s for examination of protons in the bicycloheptene ring and a mix of 0.2 s for protons adjacent to cyclopentene vinyl protons.

Scheme 2[a]



[a] Reaction conditions: (i) CpH, pyrrolidine, MeOH, 25 °C, 18 h. (ii) LAH, Et_2O, 25 °C, 2 h. (iii) BuLi, THF, 0 °C, 30 min; $ZnCl_2$, 0 °C, 30 min; 1,8-diiodonaphthalene, CuI (1 mol %), 0 °C, 30 min. (iv) ^{t}BuOK, THF, 0 °C, 30 min; $FePy_4(SCN)_2$, 25 °C, 2 h. (v) CpZnCl, THF, CuI (5 mol %), 25 °C, 30 min. (vi) RCpZnCl, THF, CuI (17 mol %), 25 °C, 1 h.

solutions enriched in the minor isomer shows that the two substances are isomeric with respect to substitution at C-5 and C-6 in the bicycloheptene ring. The minor Diels–Alder adduct must therefore have structure **13**. Thus, of the four possible Diels–Alder products, **12**–**15**, only the two derived from intermediate **10** are formed. The same results are obtained in the preparation of **6a** from diiodonaphthalene or by independent cyclopentadienlyation of **6a** itself. These relationships are shown in Scheme 3.

We found that the transformation of **6a** and **6b** to the corresponding diastereomeric mixture of ferrocenes **7a** and **7b** was best achieved using the $FePy_4(SCN)_2$ salt[8] as a source of Fe(II).[24] Cyclopentadienylation of **7a** and **7b** yielded the effective monomers **8a** and **8b**, which were then subjected to polymerization by treatment with base and either an Fe(II) or Ni(II) salt. These transformations are summarized in Scheme 2.

Exploratory polymerizations of monomers **8a**, **8b**, and **9a** were carried out in several solvents and in the presence of several different bases and salts, to examine the effect of these variables on the ferrocene polymers and ferrocene–nickelocene copolymers formed in these reactions. The results of these experiments are summarized in Tables 1 and 2. In general, yields of crude polymer obtained in the polymerization reactions were high. However, since chain growth proceeds by step condensations, involving complexation of cyclopentadienide by a partially soluble metal salt, polymerizations were relatively slow. These reactions were therefore generally carried out over a period of several days, at

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(24) This complex salt was found to be superior to $FeCl_2$ in the reaction, possibly owing to its greater solubility over the latter salt. Care must be taken in handling this material, as it is readily oxidized to the purple Fe(III) salt on standing. The oxidized salt can, however, be easily removed by washing the complex salt several times with THF before using it.

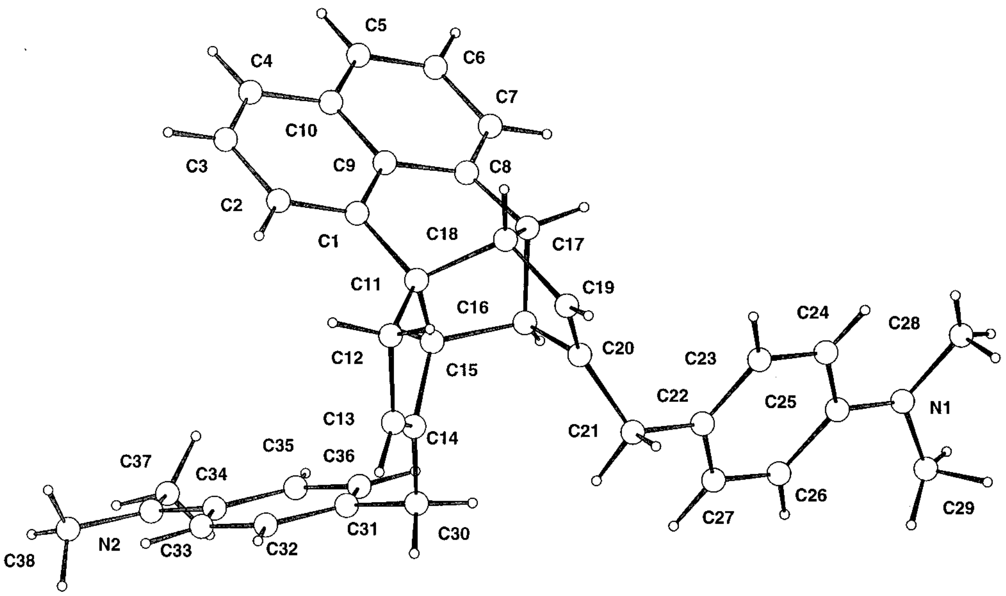
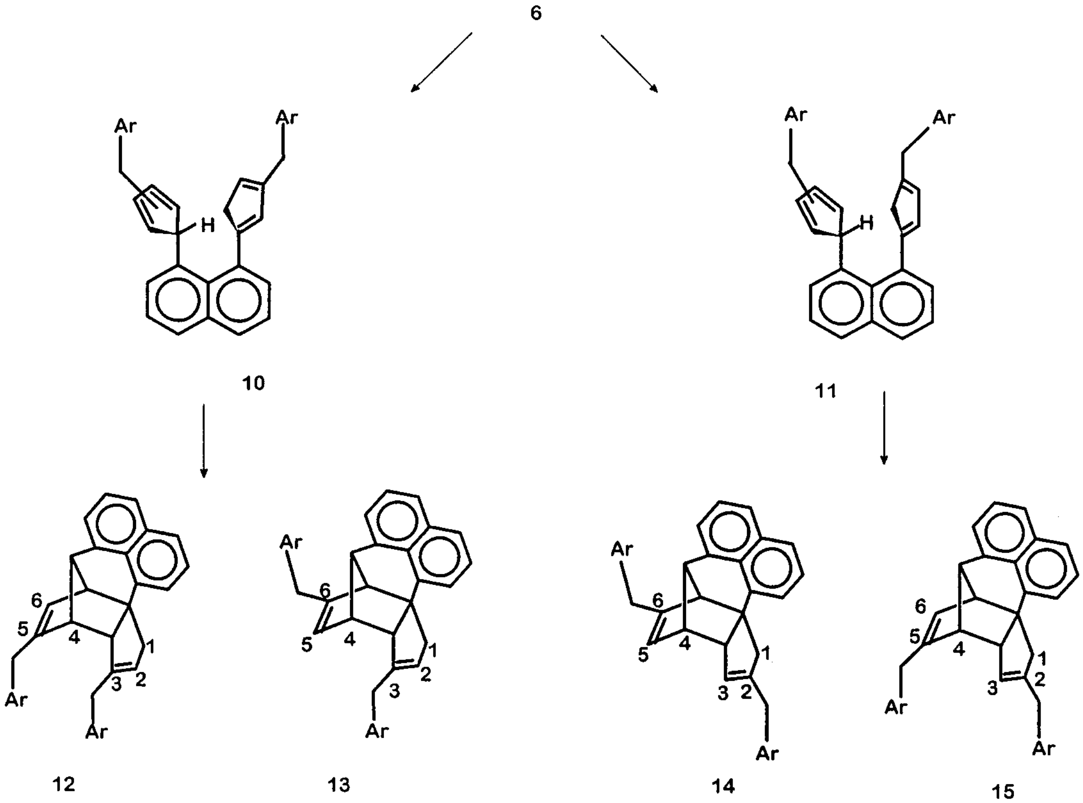


Figure 1. Molecular structure of compound **12b**.

Scheme 3



a. R=4-BnOPh
b. R=4-Me_2NPh

elevated temperatures. Thus, copolymerization of monomer **9a**, in which metal complexation is retarded by cyclopentadienyl-ring substitution, was far from complete after 3 days of reaction at room temperature. The dark brown to black polymeric products are generally insoluble in toluene, but a significant portion of these was found to be soluble in pyridine. These pyridine-soluble fractions were subjected to GPC analysis and exhibited a significantly higher molecular weight distribution and polydispersity than had been observed for the corresponding alkyl-chain-substituted polymers.[4] For example, high molecular weight ferrocene polymers **1b** (R = 2-octyl, R′ = H) typically had M_w and M_n values of 18 000 (DP_w = 21) and 14 000, respectively, after fractionation, while those derived from the polymerization of **8a** were obtained as pyridine-soluble fractions with considerably larger molecular weights and polydispersity (Table 2). In contrast to alkyl-substituted polymers, which gave amorphous solids on removal of solvent, evaporation of solvent from pyridine solutions of these higher molecular materials left a pale amber film of the polymer. The limited number of experiments involving polymerization of the 4-dimethylaminobenzyl-substituted monomer **8b** suggests that this substituent is not as effective as the 4-benzyloxybenzyl group in solubilizing ferrocene-derived polymers (Table 2). However this substituent appears to be more effective in solubilizing ferrocene−nickelocene copolymers. Thus the 2-octyl-substituted copolymer **1b**, reported earlier (M = Fe, M′ = Ni),[4] exhibited M_w and M_n of 5700 (DP_w =7) and 1500 in THF or toluene solutions and was poorly soluble in pyridine. By contrast, iron−nickel copolymers derived from monomer **8b** showed a moderate solubility in pyridine and had a significantly higher distribution of molecular weights (Table 3).

In conclusion, we have shown that cardo-substituted monomers **8a**,**b** give polymeric metallocenes which show increased solubility, especially in pyridine solutions, compared to their alkyl-chain-substituted analogues. Other members of this class of cyclic substituent may prove to be more effective.

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Supporting Information Available: CIF file containing data for the structure of **12b**. This material is available free of charge via the Internet at http://pubs.acs.org.

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