Synthesis of Face-to-Face Metallocene Polymers

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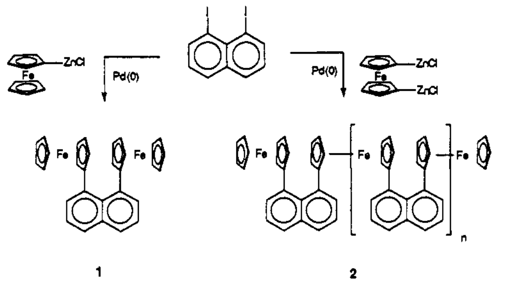
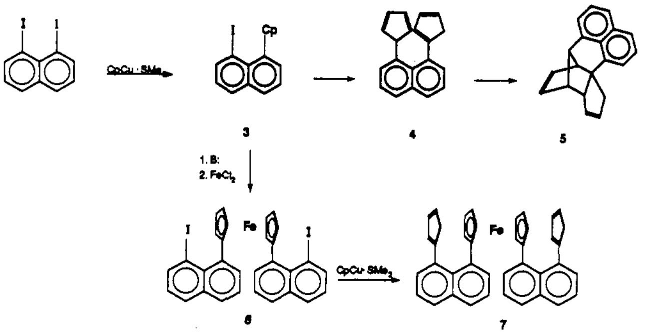
We recently reported the preparation of the first face-to-face ferrocene **1**[1] and later of related oligomeric stacked ferrocenes **2**[2] (n = 2–6) through palladium-catalyzed coupling of cholorozincferrocenes with 1,8-diiodonaphthalene. Such substances belong to a unique class of multidecked sandwich compounds,[3] of current interest for their electrical, optical, and magnetic properties.



Although low molecular weight polymers could be obtained in this metal-catalyzed polymerization reaction (M_w = 6000, M_n = 3600), the difficulty in achieving exact stoichiometry of reactants and the sensitivity of reagents makes this polycondensation polymerization route a technically difficult one to employ in the synthesis of high molecular weight material. Moreover, the synthetic methodology is not easily transferable to the synthesis of polymers incorporating other transition metals. Finally, the inherent rigidity of the molecular framework makes these polymers relatively insoluble and is undoubtedly a factor preventing the formation of higher molecular weight materials. We now report an efficient and more general methodology, which makes available much higher molecular weight, more easily processible iron as well as mixed iron–nickel polymers of this structural class.

We had earlier found that coupling of cyclopentadienylcopper dimethyl sulfide with 1,8-diiodonaphthalene led through the bis(cyclopentadienyl) **4** to the naphthalene-bridged dicyclopentadiene **5**[4] and had observed that the difference in rates of coupling for the first and second cyclopentadienyl groups were sufficiently great as to allow for the ready isolation of the intermediate 1-iodo-8-cyclopentadienylnaphthalene (**3**).[5] We were therefore led to consider the use of **3** as a polymer precursor through its transformation to the ferrocene **6** and thence to the bis(cyclopentadienyl) monomer **7**.[6]



This sequence was first modified to increase polymer solubility by introduction of a hydrocarbon chain within the monomer unit. Condensation of cyclopentadiene with 2-octanone followed by reduction of the fulvene with lithium aluminum hydride gave the cyclopentadienide,[7] which was converted to its copper salt and coupled with 1,8-diiodonaphthalene to give **8**[8] in 72% overall yield. Conversion of this to the iodoferrocene **9**[9] through treatment with sodium bis(trimethylsilyl)amide and ferrous chloride followed by coupling with cyclopentadienylcopper dimethyl sulfide gave the monomer **10a**[10] in 71% yield.

Polymerization of **10a** is readily effected by treatment with sodium hexamethylsilylamide followed by ferrous chloride. The presence of a reactive end group on the growing polymer chain is evidenced by changes in gel permeation retention volumes, which show a progressive loss of low molecular weight material and a corresponding increase in higher molecular weight components on successive addition of ferrous chloride or base. Similarly, isolation of polymer followed by resubmission to polymerization by treatment with base and ferrous chloride also resulted in an increase in higher molecular weight fractions at the expense of low molecular weight material.

Thus, prolonged reaction of **10a** at room temperature with ferrous chloride and sodium bis(trimethylsilyl)amide over a period of 10 days, during which ferrous chloride and base were periodically added, led to the formation of product, which after

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(1) Lee, M.-T.; Foxman, B. M.; Rosenblum, M. *Organometallics* **1985**, *3*, 539.

(2) Arnold, R.; Matchett, S. A.; Rosenblum, M. *Organometallics* **1988**, *7*, 2261.

(3) Grimes, R. N. *Chem. Rev.* **1992**, *92*, 251. Werner, H. *Angew. Chem., Int. Ed. Engl.* **1977**, *16*, 1. Siebert, W. *Angew. Chem., Int. Ed. Engl.* **1985**, *24*, 943. Beer, D. C.; Miller, V. R.; Sneddon, L. G.; Grimes, R. N.; Mathew, M.; Palenik, G. J. *J. Am. Chem. Soc.* **1973**, *95*, 3046. Herberich, G. E.; Büschges, U.; Dunne, B. A.; Hessner, B.; Klaff, N.; Köffer, D. P. J.; Peters, K. *J. Organomet. Chem.* **1989**, *372*, 53. Herberich, G. E.; Negele, M. *J. Organomet. Chem.* **1988**, *350*, 81. Duff, A. W.; Jonas, K.; Goddard, R.; Kraus, H.-J.; Krüger, C. *J. Am. Chem. Soc.* **1983**, *105*, 5479. Lamana, W. M. *J. Am. Chem. Soc.* **1986**, *108*, 2096. Scherer, O. J.; Schwalb, J.; Swarowsky, H.; Wolmershäuser, G.; Kaim, W.; Gross, R. *Chem. Ber.* **1988**, *121*, 443. Swann, R. T.; Hanson, A. W.; Boekelheide, V. *J. Am. Chem. Soc.* **1986**, *108*, 3324. Jutzi, P.; Siemeling, U.; Müller, A.; Bögge, H. *Organometallics* **1989**, *8*, 1744. Markle, R. J.; Pettijohn, T. M.; Logowski, J. J. *Organometallics* **1885**, *4*, 1529. Bush, B. F.; Lagowski, J. J. *Organometallics* **1988**, *7*, 1945. Hopf, H.; Dannheim, J. *Angew. Chem., Int. Ed. Engl.* **1988**, *27*, 701. Kasahara, A.; Izumi, T.; Yoshida, Y.; Shimizu, I. *Bull. Chem. Soc. Jpn.* **1982**, *55*, 1901.

(4) Gronbeck, D. A.; Matchett, S. A.; Rosenblum, M. *Tetrahedron Lett.* **1989**, *30*, 2881.

(5) Gronbeck, D. A.; Matchett, S. A.; Rosenblum, M. *Tetrahedron Lett.* **1990**, *31*, 4977.

(6) The preparation of **7** and its conversion to a trinuclear mixed ferrocene–cymantrene complex has been reported (ref 5).

(7) Hafner, K. *Chem. Ber.* **1957**, *60*, 79.

(8) Anal. Calcd for $C_{23}H_{27}I$: C, 64.18; H, 6.27. Found: C, 64.67; H, 6.45. PMR analysis shows that the coupling product **8** is a mixture (2:1) of 1-aryl-3-(2-octylcyclopentadienyl) (major) and 1-aryl-4-(2-octylcyclopentadienyl) (minor) isomers. In order to simplify the structure drawings, only the major isomer is depicted here and in subsequent structures.

(9) ^{1}H 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, Fc) 6.98–7.13 (m, 4H, ArH), 7.56–7.61 (dd, 2H, J = 8.1 Hz and 1.2 Hz, ArH), 7.78–7.82 (dd, 2H, J = 8.1 and 1.2 Hz, ArH), 8.08–8.12 (dd, 2H, J = 7.5 and 1.2 Hz, ArH), 8.15–8.22 (m, 2H, ArH). ^{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 **8** to **9**. This monoiodo impurity could not be separated from **9** and results in low C values for **10a** and **10b**.

(10) ^{1}H 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, 2H, $CpCH_2$), 2.75–2.88 (m, 2H, $CpCH_2$), 3.5–4.0 (m, 6H, Fc), 5.8–6.3 (m, 6H, CpH), 6.9–7.05 (m, 4H, ArH), 7.25–7.32 (dd, 2H, J = 7.1 and 1.5 Hz, ArH), 7.33–7.41 (m, 2H, ArH), 7.58–7.68 (m, 2H, ArH), 7.69–7.78 (dd, 2H, J = 7.1 and 1.5 Hz, ArH). ^{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. Anal. Calcd for $C_{56}H_{62}Fe$: C, 85.06; H, 7.84. Found: C, 83.66; H, 7.79.

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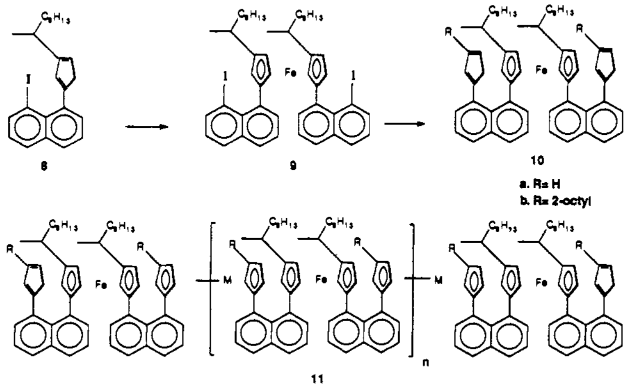

8 **9** **10**

a. R= H
b. R= 2-octyl

11

a. M=Fe, R=H
b. M=Fe, R=2-octyl
c. M=Ni, R=H

extraction with ether and methanol to remove lower molecular weight components and $FeCl_2$ gave in 71% yield a dark purple polymer (**11a**),[11] soluble in THF, with M_n = 14 363[12] and M_w = 18 398 (bimodal GPC trace peaks at 26 574 and 17 584). End-group analysis gave M_n = 18 000.[13] The proton NMR spectrum of the polymer shows very broad resonance signals at δ 6.8–7.8, 5.8–6.2, 3.5–4.0, and 0.8–1.4 for aromatic, terminal cyclopentadienyl vinyl, ferrocenyl, and aliphatic protons, respectively. When polymerization was carried out in refluxing THF for 3 days, a polymer, which was largely insoluble in THF, was obtained.

Polymerization of the fully alkylated monomer **10b**[14] proceeded more slowly, yielding polymer which on fractionation resulted in the isolation (40%) of high molecular weight polymer **11b**,[15] which was partially soluble in THF. GPC analysis of this fraction in THF showed a bimodal molecular weight distribution, with components of 139 000 molecular weight, equivalent to a number average degree of polymerization of 260.

Iron core monomers **7** and **10** may also serve as precursors to alternating mixed metal systems. Thus, treatment of **7** successively with sodium bis(trimethylsilyl)amide and nickel acetylacetonate followed by fractionation of the product gave a dark red substance, which was largely soluble in THF. GPC analysis of this fraction showed M_n = 1785, M_w = 2968, and a bimodal peak distribution with a small component at higher molecular weight (peak at 30 449). End-group analysis gave M_n = 2400.[16] Similar polymerization of **10a** gave a higher molecular weight polymer fraction, largely insoluble in THF, with a Ni/Fe ratio (average of three analyses) corresponding to a polymer with a number average degree of polymerization of 30 (**11c**, $Fe_{32}Ni_{31}$) or greater.[17] The presence of both ferrocene and nickelocene units in this polymer is supported by an examination of its infrared spectrum, which shows absorption (CsI pellet) at 440 and 390 cm^{-1}, characteristic of M-ring stretching vibrations in the iron and nickel metallocenes, respectively.[18] Bulk magnetic suceptibility measurements on a polymer sample give a mean effective magnetic moment of 3.51 ± 0.3 μ_B for the nickelocene unit, a value close to but significantly higher than that observed for nickelocene itself,[19] providing further evidence for the presence of a nickelocene core unit in the polymer. Finally, a room temperature proton NMR spectrum of a Ni–Fe polymer shows very broad resonances centered at δ 7.5, 6.0, 4.4, and 2.6, corresponding to aromatic, vinyl, ferrocene, and aliphatic protons, respectively. A short-acquisition-time rapid recycle NMR experiment is required to observe the resonance of nickelocene Cp protons, which appears as two overlapping triplets centered at −260 ppm (width at half height ≈ 12 ppm).[20]

The synthetic methodology outlined above lends itself readily to functionalization of either the naphthalene or cyclopentadienyl nuclei, to further permutations involving the metal core, and to the preparation of block polymers. Further improvement in polymer processability as well as the synthesis of more elaborately functionalized polymers and an examination of their optical, electrical, and magnetic properties is in progress.

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Supplementary Material Available: Experimental details for the preparation of **8**, **9**, **10a**, **10b** and polymers **11a**, **11b** and **11c**; GPC traces of **11a** (THF-soluble fraction), **11b** (fraction partially soluble in THF), and the THF-soluble fraction of the Ni–Fe polymer derived from monomer **7** (12 pages). Ordering information is given on any current masthead page.

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(11) Anal. Calcd for $[C_{56}H_{61}Fe_2(C_{56}H_{60}Fe_2)_nC_{56}H_{61}Fe]$ (n = 10–100): Fe, 12.74–13.21. Found: Fe, 13.67; I, 0.00.

(12) Molecular weights were determined by gel permeation chromatography using 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 four narrow band molecular weight polystyrene standards ranging from M_n 500 to 20 000. The sample was dissolved in He-degassed HPLC grade THF at a concentration of 0.5% w/v and monitored at a flow rate of 1.0 mL/min.

(13) End-group analysis was carried out by measuring the ratio of integrated areas for terminal proton resonances of vinyl cyclopentadienyl to aryl and to ferrocenyl plus aliphatic proton signals. These gave values of M_n of 18 000 and 17 700, respectively.

(14) ^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, Fc), 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, 128.79, 130.86, 131.29, 133.81. Anal. Calcd for $C_{72}H_{44}Fe$: 85.20; H, 9.27. Found: C, 82.06; H, 8.85.

(15) Anal. Calcd for $[C_{72}H_{93}Fe_2(C_{72}H_{92}Fe_2)_nC_{72}H_{93}Fe]$ (n = 10–300): Fe, 10.09–10.90. Found: Fe, 10.09; I, 0.00.

(16) End-group analysis was carried out by determining the ratio of integrated areas for aromatic or ferrocenyl proton resonances to terminal cyclopentadienyl vinyl or methylene signals. These give an average value of 2410 ± 200.

(17) The calculated Fe/Ni ratio and the %Ni are not very sensitive to the number average degree of polymerization beyond a value of 30, corresponding to a polymer with Fe/Ni = 32/31. 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, 6.38–6.90. Found: Fe, 6.63; Ni, 6.94; I, 0.16. Ni/Fe calcd for n = 10–100: 0.96–1.04. Found: 1.04.

(18) Lippincott, E. R.; Nelson, R. D. *Spectrochim. Acta* **1958**, *10*, 307. The all-iron polymer shows absorption at 430 cm^{-1}.

(19) Corrected for diamagnetic contributions from the ferrocene and naphthalene units. The effective magnetic moment of nickelocene is 2.89 ± 0.15 μ_B. Jolly, P. W.; Wilke, G. *The Organic Chemistry of Nickel*; Academic Press: New York, 1974; Vol. 1, p 424.

(20) Electron spin-lattice relaxation time for the polymer is evidently longer than that for nickelocene itself, where the single proton resonance occurs at δ 254.8 (ref 19, p 426).