Synthesis and Structure of 2,2′-Binaphthalenediyl-Substituted Ferrocenes and Derived Oligomers

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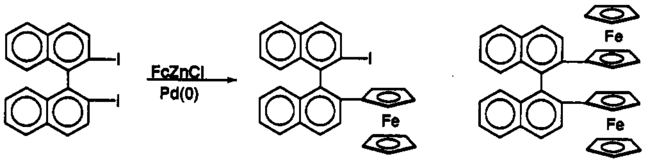
Coupling of ferrocenylzinc chloride with 2,2′-diiodo-1,1′-binaphthyl (1), catalyzed by Pd(0), yields 2,2′-diferrocenyl-1,1′-binaphthyl (3) and 2-ferrocenyl-2′-iodo-1,1′-binaphthyl (2). Similar coupling of 1,1′-bis(chlorozincio)ferrocene with 1 yields 2,2′-(1,1′-ferrocenediyl)-1,1′-binaphthyl (4), together with oligomers, of which the triferrocenyl- and tetraferrocenyl-substituted binaphthyls 5 and 6 have been isolated and characterized. Crystals of 3 ($C_{40}H_{30}Fe_2$) are monoclinic, space group $P2_1/n$, with a = 14.961(5) Å, b = 11.030(5) Å, c = 18.820(5) Å, β = 110.98(3)°, and Z = 4. The molecular structure of 3 shows an unusual distortion, which is attributed to packing effects. Crystals of 4 ($C_{30}H_{20}Fe$) are monoclinic, space group $I2/a$, with a = 23.493(9) Å, b = 7.099(3) Å, c = 25.385(10) Å, β = 105.84(4)°, and Z = 8. The dihedral angle between the cyclopentadienyl rings in 4 is 12.3(3)°.

Our interest in the synthesis of organometallic polymers in which metallocene segments are held face-to-face through their *peri*-substitution on a naphthalene spacer[1] prompted us to examine the synthesis of related polymers in which a 2,2′-disubstituted 1,1′-binaphthyl unit would serve as the repeat spacer group. Mixed-valent polymers derived from such a structure could in principle exhibit charge delocalization either through a face-to-face interaction of adjoining metallocene units or through the binaphthyl framework. Moreover, since the binaphthyl spacer is obtainable in optically active form,[2] electron or spin transfer as well as nonlinear optical effects[3] for such a system would then take place in a helically asymmetric environment, and the physical properties of such polymers might therefore be of interest. Our interest in this class of compound was prompted by the elegant work of Katz[4] and his group, who have reported the preparation and properties of oligomeric cobaltocenes based on optically active heptahelicene. We report here initial results directed toward the preparation of polymetallocenes based on 2,2′-bis(cyclopentadienyl)-1,1′-binaphthyl.

We had earlier found that the introduction of ferrocenyl groups, even in sterically crowded situations, could be achieved through the coupling of aryl halides with a ferrocenylzinc halide in the presence of nickel or palladium catalysts. These reactions applied to 1,8-diiodonaphthalene proved to be an effective means for the preparation of 1,8-diferrocenylnaphthalene.[1a] When ferrocenylzinc chloride, prepared from bromoferrocene, was allowed to react with (±)-2,2′-diiodo-1,1′-binaphthyl (1) in the presence of freshly prepared Pd(dppf),[5] the mono- and bis-coupling products 2 and 3 were formed in 10 and 38% yields, respectively. The proton NMR spectrum of each of these compounds shows a five-proton singlet resonance in addition to four multiplet resonances near δ 4, as expected for a monosubstituted metallocene lacking a plane of symmetry, but one of these resonances appears at unusually high field (δ 3.7). Models suggest that this resonance may be assigned to one of the two cyclopentadienyl ring α protons, which lies over a distal naphthalene ring. This is supported by the molecular structure of 2,2′-diferrocenylbinaphthyl 3 (Figure 1), which shows that the protons bound to C2B and to C5A are each held over naphthalene rings A and B, respectively.



1 2 3

Inspection of Figure 1 reveals a highly unsymmetrical structure for 3. The two cyclopentadienyl moieties attached to binaphthyl have dihedral angles of 44.8 and 6.2° to naphthalene rings A and B, respectively. Dihedral angles between the cyclopentadienyl and naphthalene fragments in the sterically crowded 1,8-diferrocenylnaphthalene system[1a] average 46°. While it is not clear what the expected value should be in the present case, we sought an explanation for the apparent lack of symmetry in the nonbonded contacts for 3. An examination of intra- and intermolecular contacts suggested that this distortion arises from a short intermolecular contact, 3.34 Å, between C5B and C5B ($\bar{x}$, $\bar{y}$, $1 - z$) (see Figure 2). The dihedral

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[1] (a) Lee, M.-T.; Foxman, B. M.; Rosenblum, M. *Organometallics* **1985**, *4*, 539. (b) Gronbeck, D. A.; Matchett, S. A.; Rosenblum, M. *Tetrahedron Lett.* **1990**, *35*, 4977. (c) Foxman, B. M.; Gronbeck, D. A.; Rosenblum, M. *J. Organomet. Chem.* **1991**, *413*, 287.

[2] Brown, K. Y.; Berry, M. S.; Murdoch, J. R. *J. Org. Chem.*, **1985**, *50*, 4345.

[3] Calabrese, J. C.; Cheng, L.-T.; Green, J. C.; Marder, S. R.; Tam, W. *J. Am. Chem. Soc.* **1991**, *113*, 7227.

[4] Sudhakar, A.; Katz, T. J.; Yang, B.-W. *J. Am. Chem. Soc.* **1986**, *108*, 2790 and references therein.

[5] Pd(dppf) is dichloro-1,1′-bis(diphenylphosphino)ferrocene. Hayashi, T.; Mitsuo, K. Kobori, Y.; Kumada, M.; Higuchi, T.; Hirotsu, K. *J. Am. Chem. Soc.* **1984**, *106*, 158.

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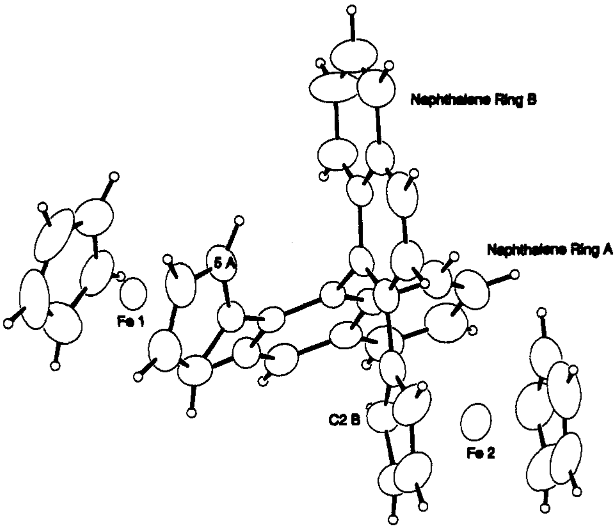


Figure 1. Molecular structure of 3, showing labeling scheme.

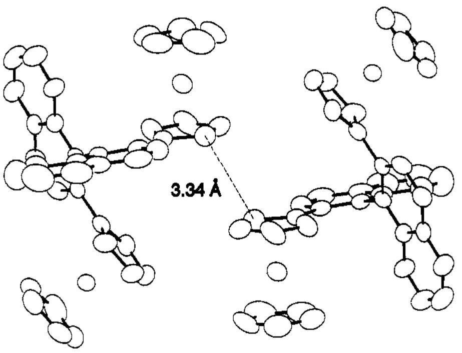


Figure 2. Two molecules of 3, showing the short intermolecular contact between C5B and C5B ($\bar{x}$, $\bar{y}$, 1 − z).

Table I. Selected Bond Lengths (Å) for $C_{40}H_{30}Fe_2$ (3)

Fe1–C1A	2.061(5)	Fe2–C1B	2.070(5)
Fe1–C2A	2.036(5)	Fe2–C2B	2.028(6)
Fe1–C3A	2.033(6)	Fe2–C3B	2.027(7)
Fe1–C4A	2.027(6)	Fe2–C4B	2.041(7)
Fe1–C5A	2.038(6)	Fe2–C5B	2.027(6)
Fe1–C6A	2.024(7)	Fe2–C6B	2.025(8)
Fe1–C7A	2.024(6)	Fe2–C7B	2.036(7)
Fe1–C8A	2.021(6)	Fe2–C8B	2.038(7)
Fe1–C9A	2.030(7)	Fe2–C9B	2.023(7)
Fe1–C10A	2.036(6)	Fe2–C10B	2.036(8)

angle between the halves of the binaphthyl moiety is 97.6(1)°. Bond lengths and angles within the ferrocene group are very close to those observed for 1,8-diferrocenylnaphthalene (Table I and supplementary data);[1a] maximum distortions within the naphthalene planes are ±0.035(5) Å, less than those observed for 1,8-diferrocenylnaphthalene (±0.171(3) Å). Other important deviations include those of the *ipso*-carbon atoms (0.139(5) and 0.021(5) Å, from planes A and B, respectively) and those of the binaphthyl 1- and 1′-carbon atoms (−0.040(5) and −0.183(5) Å, from planes A and B, respectively). A biphenyl analog of 3 was recently prepared by Brinzinger *et al.*[6] by palladium-catalyzed coupling of 2,2′-biphenyl with ferrocenylzinc chloride.

These results prompted us to examine the coupling reaction using 1,1′-bis(chlorozincio)ferrocene. In the event, treatment of 1 with the dimetalated ferrocene gave a mixture of the binaphthyl-bridged 1,1′-disubstituted ferrocene 4 (37%) together with a mixture of oligomeric compounds. As with 2 and 3, the proton NMR spectrum of 4 shows two highly shielded cyclopentadienyl protons at δ 3.35, which are assigned to the single α proton in each of the arylated cyclopentadienyl rings. These protons are held rigidly within the shielding region of the naphthalene ring to which they are not directly bonded. Brinzinger *et al.*[6] have reported the preparation of a similarly bridged ferrocene through palladium-catalyzed coupling of 1,1′-bis(chlorozincio)ferrocene with 2,2′-diiodobiphenyl; owing to poor crystal quality, details of the molecular geometry were not published.

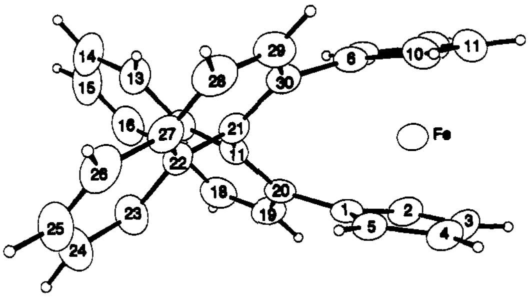
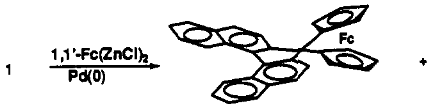


Figure 3. Molecular structure of 4, showing labeling scheme.



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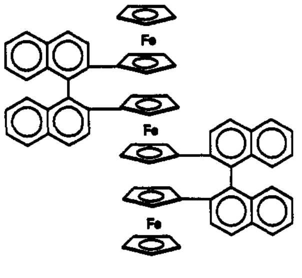

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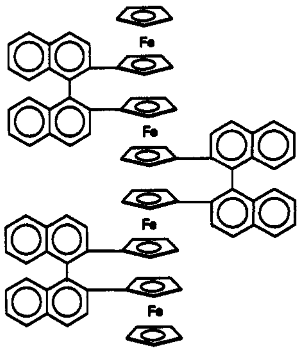

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Compound 4 is an orange crystalline substance which decomposes between 250 and 300 °C. The molecular structure of 4 (Figure 3) is quite distorted; the "splay" angle between the cyclopentadienyl rings is 12.3(3)°. This is comparable to that (13.8°) observed for 1,1′-(1,8-naphthalenediyl)ferrocene,[7] a three-carbon-bridged ferrocene, and the four-carbon bridged molecule 1,4-(1,1′-ferrocenediyl)-1,3-butadiene (10.7°).[8] The dihedral angle between the halves of the binaphthyl moiety is 74.2(2)°; for comparison, the torsion angle about the central bond of the butadiene in 1,4-(1,1′-ferrocenediyl)-1,3-butadiene is 42.2°. Iron–carbon lengths are slightly longer than those observed for 1,1′-(1,8-naphthalenediyl)ferrocene (Table II and supplementary data).[7] Figure 4 shows part of the crystal structure of 4, which consists of infinite chains of molecules stacked along the crystallographic *b* direction. Partial overlap of the cyclopentadienyl rings occurs in this stack, with a short intermolecular contact of 3.30 Å [C2–

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(6) Huttenloch, M. E.; Diebold, J.; Rief, U.; Brinzinger, H. H.; Gilbert, A. M.; Katz, T. J. *Organometallics* **1992**, *11*, 3601.

(7) Foxman, B. M.; Gronbeck, D. A.; Khrushchova, N.; Rosenblum, M. *J. Org. Chem.*, in press.

(8) Erickson, M. S.; Fronczek, F. R.; McLaughlin, M. L. *Tetrahedron Lett.* **1993**, *34*, 197.

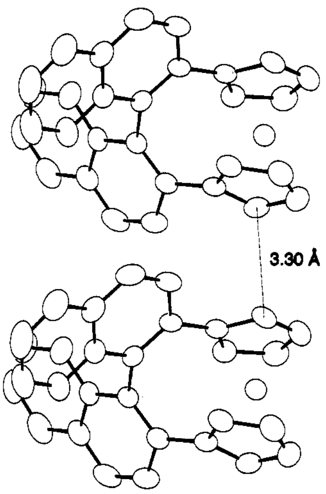

Figure 4. Two molecules of 4, showing the short intermolecular contact between C2 and C10 (*x*, 1 + *y*, *z*).

Table II. Selected Bond Lengths (Å) for $C_{30}H_{20}Fe$ (4)

Fe–C1	2.001(3)	Fe–C6	2.008(3)
Fe–C2	2.037(3)	Fe–C7	2.017(3)
Fe–C3	2.065(3)	Fe–C8	2.051(3)
Fe–C4	2.062(3)	Fe–C9	2.066(3)
Fe–C5	2.018(3)	Fe–C10	2.041(3)

C10 (*x*, 1 + *y*, *z*)]. Maximum distortions within the naphthalene planes are ±0.067(3) Å; other important deviations include those of the *ipso*-carbon atoms (0.308(3) and −0.387(3) Å, for atoms C1 and C6, respectively) and those of the binaphthyl 1- and 1′-carbon atoms (0.225(3) and −0.255(3) Å, for atoms C11 and C21, respectively).

In addition to the bridged ferrocene 4, the reaction mixture contained higher molecular weight oligomeric components. A careful chromatographic separation of these, followed by fractional crystallization, led to the isolation of 5 (10%) as a mixture of diastereomers, as indicated by the presence of two terminal cyclopentadienyl proton resonances of nearly equal intensities in its NMR spectrum. These isomers could be partially separated into a relatively pure diastereomer, dec pt >250 °C, and a second, more soluble isomer, mp 125–130 °C, only partially separated from the first. In accord with the triferrocene structure 5, the proton spectra of each of these diastereomeric oligomers show seven of the anticipated eight ring-substituted cyclopentadienyl proton resonances, in addition to a singlet resonance for the terminal cyclopentadienyl ring. These assignments are confirmed by mass spectra, which show peaks at *m*/*z* 1059.8 and 1059.2 for the individual diastereomers. Proton NMR spectral end group analyses (binaphth/terminal Cp and arylCp/terminal Cp) are also in accord with the assignment of structure 5 to these compounds. These isomers must differ only in the absolute configurations of the two chiral binaphthyl units.

In addition to these compounds, a slower-moving material proved to be a mixture of diastereomeric tetraferrocene oligomers 6 (5%), which could not be separated. A mass spectrum of this material showed a parent peak at *m*/*z* 1496.2, in accord with structure 6. The presence of at least two of the four possible diastereomers having this structure is evident from the proton NMR spectrum, which exhibits two singlet resonances for the unsubstituted cyclopentadienyl ring protons. Smaller fractions of oligomers with mass spectrometrically determined molecular weights of 807, 887, 1312, and 1244 were also isolated but were not further characterized.

An examination of this and other methods for the preparation of related polymers incorporating other metallocenes is being pursued.

Experimental Section

THF was freshly distilled from sodium benzophenone ketyl prior to use. TMEDA and hexane were distilled from Na prior to use.

2,2′-Diamino-1,1′-binaphthyl, bromoferrocene,[9] and Pd(dppf)Cl_2[10] were prepared according to literature methods. Extra dry $ZnCl_2$ was prepared from pure commercial $ZnCl_2$ (99.99%, Aldrich) by stirring at room temperature for 40 h with oxalyl chloride which had been freeze–pump–thaw-degassed three times. Oxalyl chloride was then removed *in vacuo* and the $ZnCl_2$ stored in a drybox. Finally, before each reaction, it was heated in vacuo at 150 °C for at least 3 h.

Mass spectra were obtained by matrix-assisted laser desorption ionization time-of-flight mass spectrometry, using a nitrogen laser (337 nm) on a Vestec VT2000 instrument. The mass assignment error in the molecular weight range of compounds determined is ±1 u.

2,2′-Diiodo-1,1′-binaphthyl. The following procedure represents an improvement over that given by Brown, Berry, and Murdoch,[2] using the nitrosation procedure reported recently by Kanakarajian, Haider, and Czarnik.[11] A solution of 2,2′-diamino-1,1′-binaphthyl (6 g, 20 mmol) in 100 mL of CF_3COOH was cooled to 0 °C and stirred while $NaNO_2$ (5 g, 70 mmol) was added in portions, keeping the temperature below 5 °C. After the addition was complete, the reaction mixture was stirred for an additional 15 min at 0 °C and was then poured into a solution of potassium iodide (10 g, 60 mmol) in 400 mL of water. The solution was extracted with methylene chloride, and the organic phase was washed three times with water, twice with a 10% solution of $NaHCO_3$, then twice with a saturated solution of sodium thiosulfate, and finally with water. The organic extract was dried over magnesium sulfate, and solvent was removed, leaving 9.5 g of product. This was chromatographed on a short silica gel column using carbon tetrachloride. Sublimation of the product isolated at 185 °C/0.4 mm gave 6.6 g of diiodide (62%) as a light yellow solid: mp 220–222 °C (lit.[2] mp 215.5–217.5 °C); ^{1}H NMR δ 7.07 (d, *J* = 8.1 Hz, 2H), 7.28 (m, 2H), 7.50 (m, 2H), 7.71 (d, *J* = 8.8 Hz, 2H), 7.92 (d, *J* = 8.1 Hz, 2H), 8.06 (d, *J* = 8.7 Hz, 2H).

Coupling of Ferrocenylzinc Chloride and Diiodobinaphthyl.[1a] A solution of bromoferrocene (0.41 g, 1.55 mmol) in 5 mL of hexane was cooled to 0 °C, and *n*-butyllithium (0.73 mL, 2.5 M solution in hexane, 1.83 mmol) was added. The reaction mixture was stirred at room temperature for 5 h, during which an orange precipitate formed. Hexane was removed in vacuo, and the lithiated ferrocene was dissolved in 5 mL of THF. A solution of $ZnCl_2$ (0.25 g, 1.84 mmol) in 5 mL of THF was added to this. The solution was stirred for 1 h at room temperature and was then added to a suspension of diiodobinaphthyl (0.172 g, 0.34 mmol) and Pd(dppf)Cl_2 (0.026 g, 0.036 mmol) in 5 mL of THF. The color of the reaction mixture immediately turned dark. The reaction mixture was stirred for 20 h at room temperature and then poured into 50 mL of saturated ammonium chloride solution. The solution was extracted with ether, and the combined ether extracts were dried over $MgSO_4$. Solvent was evaporated, and the products were separated on preparative silica gel plates, using 10% methylene chloride in hexane, to give 0.028 g (15%) of 2-ferrocenyl-2′-iodo-1,1′-binaphthyl (2) and 0.08 g (38%) of 2,2′-diferrocenyl-1,1′-binaphthyl (3), both as orange solids. 2: mp 207–209 °C (recrystallized from hexane); ^{1}H NMR δ 3.67 (m, 1H, α-Cp), 3.95 (m, 1H, Cp α), 4.01 (m, 6H, Cp and Cp β), 4.16 (m, 1H, Cp β), 6.97 (d, *J* = 8.7 Hz, 1H), 7.2 (m, 3H), 7.44 (m, 2H), 7.66 (d, *J* = 8.8 Hz, 1H), 7.95 (m, 6H). Anal. Calcd for $C_{30}H_{21}FeI$: C, 63.86; H, 3.75. Found: C, 63.35; H, 3.76. 3:

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[9] Fish, R. W.; Rosenblum, M. *J. Org. Chem.* **1965**, *30*, 1253.

[10] Hayashi, T.; Konishi, M.; Kobori, Y.; Kumada, M.; Higuchi, T.; Hirotsu, K. *J. Am. Chem. Soc.* **1986**, *106*, 158.

[11] Kanakarajian, K.; Haider, K.; Czarnik, A. W. *Synthesis* **1988**, 567.

Table III. Data for the X-ray Diffraction Study of 3 and 4

	$C_{40}H_{30}Fe_2$ (**3**)	$C_{30}H_{20}Fe$ (**4**)
(A) Crystal Data at 21(1) °C		
crystal system	monoclinic	monoclinic
space group	$P2_1/n$ (C^5_{2h}; No. 14)	$I2/a$ (C^6_{2h}; No. 15)
a, Å	14.961(5)	23.493(9)
b, Å	11.030(3)	7.099(3)
c, Å	18.820(6)	25.385(10)
β, deg	110.98(3)	105.84(4)
V, Å^3	2899.8(33)	4072.9(57)
Z	4	8
crystal size, mm	0.084 × 0.38 × 0.71	0.15 × 0.25 × 0.63
fw	622.38	436.34
ρ_{calcd}, g cm^{-3}	1.426	1.423
μ, cm^{-1} (Mo Kα)	10.3	7.53
cell constant determination	seven pairs of $\pm(hkl)$ and refined 2θ, ω, χ values in the range $23 \leq \|2\theta\| \leq 25°$ (λ(Mo Kα) = 0.710 73 Å)	
(B) Collection and Refinement of Intensity Data[a]		
radiation	Mo Kα, graphite monochromator	
reflns measd	$+h,+k,\pm l$ ($3.5 \leq 2\theta \leq 43°$)	$+h, +k, \pm l$ ($3 \leq 2\theta \leq 50°$)
scan type; speed, deg/min	ω, vble; 2.44–6.51	ω, fixed; 2.93
scan ragne	1.0°; 1.0° bkgd offset in ω	1.0°; 1.0° bkgd offset in ω
no. of reflns measd	3475; 3318 in unique set	3961; 3589 in unique set
std reflns; period	060, 600 $2,0,\overline{10}$; 100	141, $0,0,\overline{14}$, $14,0,\bar{6}$; 100
abs cor	empirical	empirical
transm factor range	0.782–1.00	0.928–1.00
data reduction; as before[a]	$p = 0.040$	$p = 0.040$
R_{av}	0.025 (0kl reflns)	0.014 (0kl reflns)
no. data used in refinement	2265 [$I > 1.96\sigma(I)$]	2682 [$I > 1.96\sigma(I)$]
no. of refined params	379	281
weighting of reflns: as before[b]	$p = 0.04$	$p = 0.04$
solution	Patterson, difference-Fourier	Patterson, difference-Fourier
refinement[c]	full-matrix least-squares	full-matrix least-squares
anisotropic disp params	all non-H atoms	all non-H atoms
isotropic disp params	fixed H atoms	fixed H atoms
R	0.045	0.038
R_w	0.045	0.043
SDU	1.24	1.27
R(*all* reflections)	0.100	0.072
secondary extinction param	none	$6.4(3) \times 10^{-7}$
final diff map	four peaks, 0.26–0.28 e/Å^3 near Fe and Cp C atoms; other peaks random, in range –0.13 to +0.26 e/Å^3	five peaks, 0.20–0.26 e/Å^3 near Fe and naphthalene C atoms; other peaks random, in range –0.11 to +0.20 e/Å^3

[a] Foxman, B. M.; Goldberg, P. L.; Mazurek, H. *Inorg. Chem.* **1981**, *20*, 4368. All computations in the present work were carried out using the Enraf–Nonius Structure Determination package. [b] Corfield, P. W. R.; Doedens, R. J.; Ibers, J. A. *Inorg. Chem.* **1967**, *6*, 197. [c] $R_{av} = \sum|I - I_{av}|/\sum I$; $R = \sum||F_o| - |F_c||/\sum|F_o|$; $R_w = [\sum w(|F_o| - |F_c|)^2/\sum w|F_o|^2]^{1/2}$; SDU $= [\sum w(|F_o| - |F_c|)^2/(m - n)]^{1/2}$, where m is the number of observations and n is the number of parameters.

mp 267.7–269.5 °C (recrystallized from hexane); ^{1}H NMR δ 3.69 (m, 2H, Cp α), 3.90 (m, 10H, Cp), 3.93 (m, 2H, Cpα), 3.98 (m, 2H, Cp β), 4.22 (m, 2H, Cp β), 7.02 (d, J = 8.4 Hz, 2H, H-8), 7.17 (t, J = 3.6 Hz, 2H, H-7), 7.37 (t, J = 3.6 Hz, 2H, H-6), 7.92 (m, 6H, H-5,4,3); ^{13}C NMR δ 68.5, 68.7, 69.3, 69.5, 84.4, 125.3, 126.2, 126.4, 127.4, 127.7, 127.9, 131.9, 133.3, 133.6, 136.2. Anal. Calcd for $C_{40}H_{30}Fe_2$: C, 77.20; H, 4.86. Found: C, 77.57; H, 4.89.

Coupling of 1,1′-Bis(chlorozincio)ferrocene and Diiodobinaphthyl.[12] Butyllithium in hexane solution (4.08 mL, 10.2 mmol) was added to a suspension of ferrocene (0.84 g, 4.5 mmol) in 10 mL of hexane, followed by addition of TMEDA (1.54 mL, 10.2 mmol). The reaction mixture was stirred for 24 h at room temperature, yielding an orange precipitate. Hexane was removed by cannula, the dilithiated ferrocene was dissolved in 10 mL of THF, and the resultant solution was added to the solution of $ZnCl_2$ (1.39 g, 10.2 mmol) in 10 mL of THF. The reaction mixture was stirred for 1 h and then added to a suspension of DIBN (0.984 g, 1.94 mmol) and Pd(dppf)Cl_2 (0.146 g, 0.2 mmol) in 10 mL of THF. The resulting dark reaction mixture was stirred for 72 hours, then poured into 100 mL of a 10% solution of HCl, and extracted twice with ether and once with methylene chloride, and the extract was dried over magnesium sulfate. After removal of solvent, the residue, taken up in 15 mL of methylene chloride, was chromatographed on a short column of silica gel, eluting first with 300 mL of hexane, then with hexane/methylene chloride (5:1), and finally with methylene chloride. The product obtained from the hexane eluate was washed twice with 3 mL of hexane to remove ferrocene and was then crystallized from hexane to give 2,2′-(1,1′-ferrocenediyl)-1,1′-binaphthyl (**4**) as a mixture with a small amount of biferrocenyl. The hexane/methylene chloride eluate was evaporated to dryness, and the residue was chromatographed on preparative silica gel plates, using a 15% solution of methylene chloride in hexane. The principal product was **4**. A second fraction yielded **3** (0.038 g, 3%), and a third fraction yielded a mixture of **5** and **6**. The methylene chloride eluate was evaporated to dryness, and the residue was rechromatographed on a preparative silica gel plate using a 33% solution of methylene chloride in hexane. A small amount of **4** was isolated. The main products were identified as a mixture of **5** and **6** (0.04 g). The methylene chloride eluate above was rechromatographed on a preparative silica gel plate using a 33% solution of methylene chloride in hexane. A small amount of **4** was isolated from this fraction also. The main products were identified as oligomer **5**, as a mixture of two diastereomers (0.105 g, 10.2%), and oligomer **6** (0.028 g, 2.9%). **6**: ^{1}H NMR δ 3.14–4.22 (m), 3.82 (s), 3.84 (s), 3.92 (s), 6.87–7.96 (m); mass spectrum m/z 1496.2 (calcd 1495). End group analysis of the integrated resonances for naphthalene, aryl-substituted cyclopentadienyl, and terminal cyclopentadienyl groups gave naphth/terminal Cp = 3.7 (calcd 3.6) and arylCp/terminal Cp = 2.4 (calcd 2.4). Anal. Calcd for $C_{100}H_{70}Fe_4$: C, 80.34; H, 4.72. Found: C, 80.42, 80.24; H, 4.69, 4.68. Between these two bands, a third fraction was isolated, consisting of a mixture of two oligomers whose mass spectrum showed peaks at m/z 1312 and 1244. Spectral data were not sufficient to assign a structure for these oligomers.

Samples of impure **4**, isolated from the several fractions, were combined and crystallized from hexane to give pure product (0.314 g, 37%) as orange needles: dec pt 250–300 °C; ^{1}H NMR δ 3.36

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[12] Arnold, R.; Matchett, S. A.; Rosenblum, M. *Organometallics* **1988**, *7*, 2261.

Table IV. Atomic Coordinates for $C_{40}H_{30}Fe_2$ (3)[a,b]

atom	*x*	*y*	*z*	*B*, Å^2
Fe1	–0.09770(5)	–0.48932(7)	0.34070(4)	3.07(2)
C1A	0.0015(4)	–0.3540(4)	0.3621(3)	2.9(1)
C2A	–0.0135(4)	–0.3896(5)	0.4301(3)	3.6(1)
C3A	–0.1109(4)	–0.3703(5)	0.4196(3)	4.4(2)
C4A	–0.1561(4)	–0.3241(5)	0.3463(4)	4.3(2)
C5A	–0.0885(4)	–0.3144(5)	0.3101(3)	3.9(2)
C6A	–0.0526(4)	–0.6367(5)	0.3004(4)	4.9(2)
C7A	–0.1364(5)	–0.5909(6)	0.2449(3)	5.6(2)
C8A	–0.2070(4)	–0.5978(6)	0.2763(4)	6.8(2)
C9A	–0.1694(5)	–0.6437(6)	0.3486(4)	7.5(2)
C10A	–0.0732(5)	–0.6691(5)	0.3630(4)	6.1(2)
C11A	0.0962(3)	–0.3577(4)	0.3520(3)	2.5(1)
C12A	0.1558(4)	–0.4592(5)	0.3797(3)	3.3(1)
C13A	0.2438(4)	–0.4645(5)	0.3758(3)	3.5(1)
C14A	0.2810(4)	–0.3682(5)	0.3458(3)	3.0(1)
C15A	0.3738(4)	–0.3698(6)	0.3434(3)	4.2(2)
C16A	0.4079(4)	–0.2734(6)	0.3172(3)	5.1(2)
C17A	0.3499(4)	–0.1714(6)	0.2892(3)	4.8(2)
C18A	0.2594(4)	–0.1677(5)	0.2891(3)	4.0(1)
C19A	0.2217(4)	–0.2651(5)	0.3175(3)	2.9(1)
C20A	0.1284(3)	–0.2616(4)	0.3221(3)	2.6(1)
Fe2	0.23490(6)	0.04057(7)	0.48327(5)	4.08(2)
C1B	0.1145(4)	–0.0623(5)	0.4273(3)	3.4(1)
C2B	0.1925(4)	–0.1353(5)	0.4731(3)	4.3(2)
C3B	0.2213(5)	–0.0977(6)	0.5497(3)	5.4(2)
C4B	0.1628(4)	–0.006(7)	0.5540(3)	5.9(2)
C5B	0.0986(4)	0.0227(6)	0.4799(3)	5.2(2)
C6B	0.3474(4)	0.0529(7)	0.4479(4)	6.5(2)
C7B	0.3746(5)	0.0931(8)	0.5239(4)	7.1(2)
C8B	0.3166(5)	0.1901(6)	0.5258(4)	7.3(2)
C9B	0.2528(5)	0.2108(6)	0.4506(5)	8.1(3)
C10B	0.2738(5)	0.1267(7)	0.4031(4)	6.8(2)
C11B	0.0597(3)	–0.0629(5)	0.3441(3)	3.1(1)
C12B	–0.0061(4)	0.0327(5)	0.3139(3)	4.1(2)
C13B	–0.0612(4)	0.0383(5)	0.2399(4)	4.8(2)
C14B	–0.0523(3)	–0.0464(5)	0.1872(3)	3.8(1)
C15B	–0.1072(4)	–0.0406(6)	0.1079(4)	5.9(2)
C16B	–0.0956(5)	–0.1241(7)	0.0609(4)	7.2(2)
C17B	–0.0302(5)	–0.2180(7)	0.0864(4)	6.8(2)
C18B	0.0232(4)	–0.2276(6)	0.1628(3)	4.8(2)
C19B	0.0136(4)	–0.1424(5)	0.2148(3)	3.2(1)
C20B	0.0678(3)	–0.1514(4)	0.2948(3)	2.7(1)

[a] Atoms refined using anisotropic displacement parameters are given in the form of the isotropic equivalent displacement parameter defined as $1.33[a^2B_{11} + b^2B_{22} + c^2B_{33} + ab(\cos\gamma)B_{12} + ac(\cos\beta)B_{13} + bc(\cos\alpha)B_{23}]$. [b] Numbers in parentheses in this and the following table are estimated standard deviations in the least significant digit.

(m, 2H, Cp α), 4.04 (m, 2H, Cp α), 4.46 (m, 2H, Cp β), 4.58 (m, 2H, Cp β), 6.84 (d, J = 8.5 Hz, 2H, H-8), 7.06 (t, J = 8.5 Hz, 2H, H-7), 7.36 (t, J = 8.5, 2H, H-6), 7.70 (d, J = 8.6 Hz, 2H, arom), 7.89 (m, 4H, arom); ^{13}C NMR δ 68.8, 69.0, 73.9, 78.7, 83.0, 125.1, 126.0, 126.1, 126.5, 127.9, 128.0, 132.9, 133.3, 134.9, 136.2. Anal. Calcd for $C_{30}H_{20}Fe$: C, 82.58; H, 4.62. Found: C, 82.73; H, 4.36.

Fractional crystallization of 0.105 g of **5** obtained above from benzene/pentane gave a less soluble diastereomer, which was filtered off, washed twice with a small amount of chloroform, and recrystallized from CH_2Cl_2/hexane, to give 0.01 g of pure diastereomer: dec pt 250–300 °C; mass spectrum *m/z* 1059.8 (calcd 1058.7); ^{1}H NMR δ 3.37–4.08 (m, 16H, Cp), 3.85 (s, 10H, terminal Cp), 6.9–7.95 (m, 24H, arom). An end group analysis, carried out by determining the integrated resonances for the terminal cyclopentadienyl and arylcyclopentadienyl ring protons, as well as the naphthalene protons, gave the following: naphth/terminal Cp = 2.6 (calcd 2.4), arylCp/terminal Cp = 1.5 (calcd 1.6). Anal. Calcd for $C_{70}H_{50}Fe_3$: C, 79.44; H 4.76. Found: C, 78.77; H, 6.01. The second diastereomer was obtained from the benzene/pentane solution as a mixture with a small amount of the first diastereomer, after recrystallization from hexane: mass spectrum *m/z* 1059.2; ^{1}H NMR δ 3.33–4.18 (m, 16H, Cp), 3.86 (s, 10H, terminal Cp), 7.9–8.0 (m, 24H, arom). End group analysis as above: naphth/terminal Cp = 2.6, RCp/terminal Cp = 1.8. Anal. Calcd for $C_{70}H_{50}Fe_3C_6H_{14}$: C, 79.73; H, 5.64. Found: C, 79.77, 79.29; H, 5.95, 5.87.

X-ray Structural Analysis of 3 and 4. X-ray-quality crystals of **3** and **4** were obtained by recrystallization from CH_2Cl_2/hexane solutions. The crystals were mounted on Pyrex fibers affixed to brass pins and were transferred to a Supper No. 455 goniometer and optically centered on a Syntex P2$_1$ diffractometer. Operations were performed as described previously.[13] The analytical scattering factors of Cromer and Waber were used; real and imaginary components of anomalous scattering for all atoms were included in the calculations.[14] All computational work was carried out on a VAX 6420 computer using the Enraf-Nonius MolEN package.[15] Details of the structure analyses, in outline form, are given in Table III, while atomic coordinates for **3** and **4** appear in Tables IV and V, respectively.

Table V. Atomic Coordinates for $C_{30}H_{20}Fe$ (4)[a]

atom	*x*	*y*	*z*	*B*, Å^2
Fe	0.69265(2)	0.06941(6)	0.11422(2)	2.814(8)
C1	0.7423(1)	0.3026(4)	0.1296(1)	2.60(6)
C2	0.6857(1)	0.3468(4)	0.0929(1)	3.51(7)
C3	0.6419(1)	0.3025(5)	0.1195(1)	4.00(8)
C4	0.6697(1)	0.2346(5)	0.1720(1)	3.83(7)
C5	0.7316(1)	0.2340(4)	0.1788(1)	3.03(6)
C6	0.7509(1)	–0.1426(4)	0.1219(1)	2.78(6)
C7	0.7339(1)	–0.0750(4)	0.0669(1)	3.14(6)
C8	0.6718(1)	–0.0988(5)	0.0459(1)	4.12(8)
C9	0.6503(1)	–0.1818(5)	0.0873(1)	4.32(8)
C10	0.6986(1)	–0.2102(4)	0.1337(1)	3.65(7)
C11	0.8423(1)	0.1753(4)	0.1267(1)	2.50(6)
C12	0.8888(1)	0.1775(4)	0.0998(1)	2.83(6)
C13	0.9309(1)	0.0321(5)	0.1068(1)	3.72(7)
C14	0.9744(1)	0.0352(6)	0.0796(1)	4.74(9)
C15	0.9779(1)	0.1864(7)	0.0452(1)	5.15(9)
C16	0.9385(1)	0.3277(6)	0.0375(1)	4.42(8)
C17	0.8926(1)	0.3281(5)	0.0639(1)	3.29(7)
C18	0.8493(1)	0.4698(4)	0.0546(1)	3.74(7)
C19	0.8029(1)	0.4586(4)	0.0768(1)	3.30(7)
C20	0.7982(1)	0.3110(4)	0.1129(1)	2.46(6)
C21	0.8463(1)	0.0271(4)	0.1698(1)	2.48(6)
C22	0.8929(1)	0.0482(4)	0.2195(1)	2.65(6)
C23	0.9282(1)	0.2139(5)	0.2308(1)	3.52(7)
C24	0.9716(1)	0.2345(6)	0.2790(1)	4.26(8)
C25	0.9830(1)	0.0898(6)	0.3180(1)	4.53(8)
C26	0.9502(1)	–0.0687(5)	0.3091(1)	4.17(7)
C27	0.9036(1)	–0.0940(4)	0.2600(1)	3.07(6)
C28	0.8681(1)	–0.2548(4)	0.2507(1)	3.75(7)
C29	0.8212(1)	–0.2699(4)	0.2052(1)	3.53(7)
C30	0.8086(1)	–0.1266(4)	0.1645(1)	2.72(6)

[a] Atoms refined using anisotropic displacement parameters are given in the form of the isotropic equivalent displacement parameter defined as $1.33[a^2B_{11} + b^2B_{22} + c^2B_{33} + ab(\cos\gamma)B_{12} + ac(\cos\beta)B_{13} + bc(\cos\alpha)B_{23}]$.

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Supplementary Material Available: Tables S-I–S-VIII, listing all bond lengths and angles, anisotropic displacement parameters, H atom coordinates, and least-squares planes for **3** and **4** (15 pages). Ordering information is given on any current masthead page.

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