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New Face-To-Face Metallocene Triads

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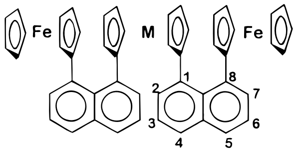
The ferrocene compound 1-cyclopentadienyl-8-ferrocenylnaphthalene (**5**) is readily available from 1,8-diiodonaphthalene and is shown to serve as a useful precursor to stacked trinuclear complexes of general structure **1**. Two new complexes of this type, an Fe−Co$^+$−Fe (**1b**) and an Fe−Ti(Cl$_2$)-Fe (**1c**) triad, in addition to the Fe−Fe−Fe triad (**1a**) previously prepared, are reported. The crystal structure of **1c** has been determined. Individual molecules are shown to adopt chiral conformations in the racemic crystal. Molecular distortions (Cp ring twisting and splaying), which are associated with electronic charge on the Cp rings, are found to be considerably greater in **1c** than in **1a**.

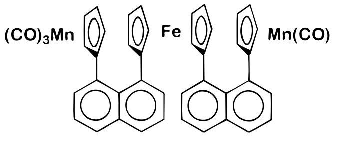
Introduction

We recently reported the preparation of trimetallic systems **1a**[2] and **2**,[3] as part of a program designed to examine intramolecular interactions in such trimetallocene systems and in structurally related polymers,[4] in which the organometallic units are constrained to a stacked arrangement. Since the synthetic methodology used for the preparation of **1a** and **2** was not readily suited for the synthesis of a broader spectrum of such model compounds, we sought a more systematic approach to stacked trimetallic metallocenes.



1

a. M=Fe
b. M=Co+
c. M=TiCl$_2$



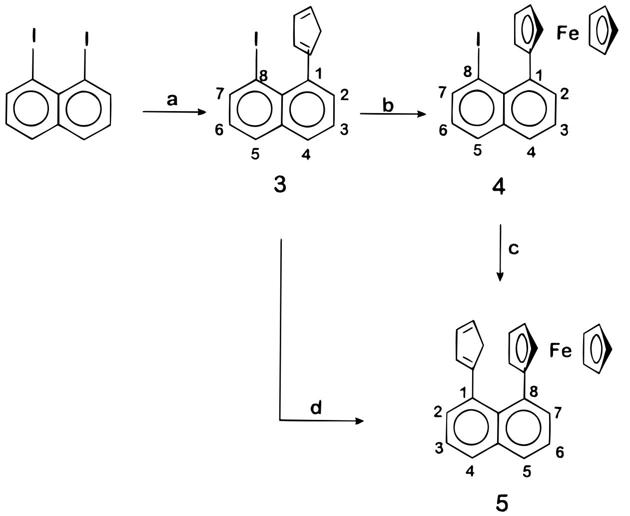
2

Herein we report the preparation of two new members of such triad models (**1b**,**c**) by a more general synthetic sequence and the crystal structure of **1c**.

Results and Discussion

The key intermediate 1-cyclopentadienyl-8-ferrocenylnaphthalene (**5**), used in the synthesis of the model triads **1**, can be prepared by several routes. In the first of these, 1-cyclopentadienyl-8-iodonaphthalene (**3**), obtained by coupling of 1,8-diiodonaphthalene with cyclopentadienylzinc chloride,[5] was converted to 1-ferrocenyl-8-iodonaphthalene (**4**) (Scheme 1). This was then coupled with cyclopentadienylzinc chloride in the presence of CuI catalyst to give **5**. However, the low yields obtained in the conversion of **3** to **4** prompted us to examine an alternate and shorter route to **5.** In this, **3** is converted to **5** in one step by coupling with ferrocenylzinc chloride in the presence of a palladium catalyst.[6] Either Pd(PPh$_3$)$_4$ or Pd(dppf)$_2$Cl$_2$[7] was found to be effective as a catalyst in the coupling reaction, but the latter required higher reaction temperatures, which led to the formation of small amounts of products **7a**,**b** (vide infra), derived from intramolecular alkylation of **5**. Ferrocenylzinc chloride used in these reactions was prepared

Scheme 1[a]



[a] Legend: (a) CpZnCl, THF, 0 °C, 3 h; (b) CpH, FePy$_4$(SCN)$_2$, KN(Me$_3$Si)$_2$, THF, −78 to 25 °C, 1.5 h; (c) CpZnCl, CuI (cat), 0−25 °C, 1 h; (d) FcZnCl$_2$, Pd(PPh$_3$)$_4$, 25 °C, 3 h.

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(5) The use of zinc reagent represents a significant improvement in these cyclopentadienyl coupling reactions, which have previously been carried out with less satisfactory copper reagents. Foxman, B. M.; Gronbeck, D. A.; Khruschova, N.; Rosenblum, M. *J. Org. Chem.* **1993**, *58*, 4078−4082.

(6) *Metal Catalyzed Cross-Coupling Reactions*; Diederich, F., Stang, P. J., Eds.; VCH-Wiley: Weinheim, Germany, 1998.

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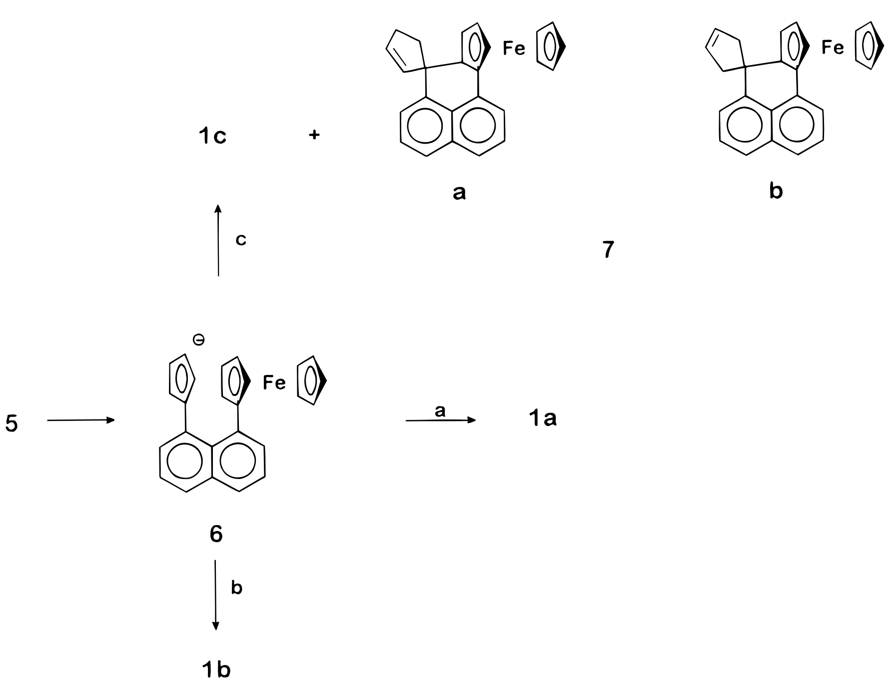
10.1021/om990750l CCC: $19.00

Scheme 2[a]



[a] Legend: (a) $NaN(SiMe_3)_2$, $FePy_4(SCN)_2$, THF, 25 °C, 2 h; (b) $NaN(SiMe_3)_2$, $CoBr_2$, THF, 1 h; (c) BuLi, $TlCl_3$, THF, −78 to 0 °C, 4 h.

from lithioferrocene, obtained either by monolithiation of ferrocene with *tert*-butyllithium under carefully controlled conditions of temperature and solvent composition[8] or more easily by lithiation of bromoferrocene[9] with butyllithium. The zinc reagent prepared by this latter route provided consistently high and easily reproducible yields of **5** in the coupling reaction.

We then prepared the trinuclear systems **1**, through conversion of **5** to its anion **6** in the presence of potassium bis(trimethylsilyl)amide, followed by reaction of this with the appropriate metal salt (Scheme 2). To examine this sequence, **6** was treated first with bis(thiocyanato)tetrakis(pyridine)iron[10] to give a product identical with the triiron compound **1a**, isolated previously from among the several products formed in the reaction of 1,1′-bis(chlorozinc)ferrocene with 1,8-diiodonaphthalene.[11] The structure of this compound had earlier been determined by X-ray crystallography.[2]

THF solutions of **6** turn black on treatment with anhydrous $CoBr_2$, consistent with the formation of a cobaltocene complex. No attempt was made to isolate the reactive neutral complex, but these solutions were instead treated with acid to promote conversion to a cobaltocenium salt. Treatment with solutions of strong acids such as HBF_4 etherate, aqueous HPF_6, perchloric acid, or trifluoroacetic acid led to immediate oxidation of the cobalt center. The resulting cobaltocenium salts were isolated by precipitation from their methylene chloride solutions with ether and were obtained as brown amorphous solids after several reprecipitations. Attempts to obtain a crystalline sample of these salts failed. Instead, the PF_6 salt was fully characterized by its proton and C-13 NMR spectra and by elemental analysis. The proton spectrum of this salt shows resonances at δ 5.16 and 5.00 typical of the cyclopentadienyl protons in cobaltocenium salts,[12] downfield from ferrocenyl protons in **1b**. These are generally observed at δ 4.04, 3.91, and 3.89 for α, β and unsubstituted cyclopentadienyl ring protons, respectively. In addition, the C-13 spectrum of the salt exhibits cyclopentadienyl resonances typical of cobaltocenium salts[13] at δ 81.8 and 84.4, as well as a signal at δ 109 for the *ipso* cyclopentadienyl carbon center. These are well downfield from the corresponding ferrocene ring resonances at δ 68.1, 70.1, 71.5, and 91.6 assigned to the β, unsubstituted, α, and *ipso* carbon centers, respectively.

Group IV metallocene dihalides and compounds derived from them by halogen replacement represent a large and readily characterizable constellation of metallocene complexes. Of these, the titanium and zirconium complexes have acquired renewed interest as catalysts in the polymerization of α-olefins.[14] Compound **5** appears to constitute a fairly hindered cyclopentadiene derivative, since attempts to convert its sodium or lithium salt to a zirconium complex through treatment with zirconium tetrachloride,[15] under varied reaction conditions of solvent, temperature, and reaction time,

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[8] Guillaneux, D.; Kagan, H. B, *J. Org. Chem.* **1995**, *60*, 2502−2505.

[9] Fish, R. W.; Rosenblum, M. *J. Org. Chem.* **1965**, *30*, 1253−1254. The Guillaneux and Kagan procedure,[8] under the best of conditions, yields mixtures of ferrocene and of mono- and dilithioferrocene, which complicates the purification procedure for **5**. To obtain pure monolithioferrocene, using the Kagan procedure, it is necessary to transform the lithio salt to the trimethylstannyl derivative, purify it, and reconvert this to the lithio salt.

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

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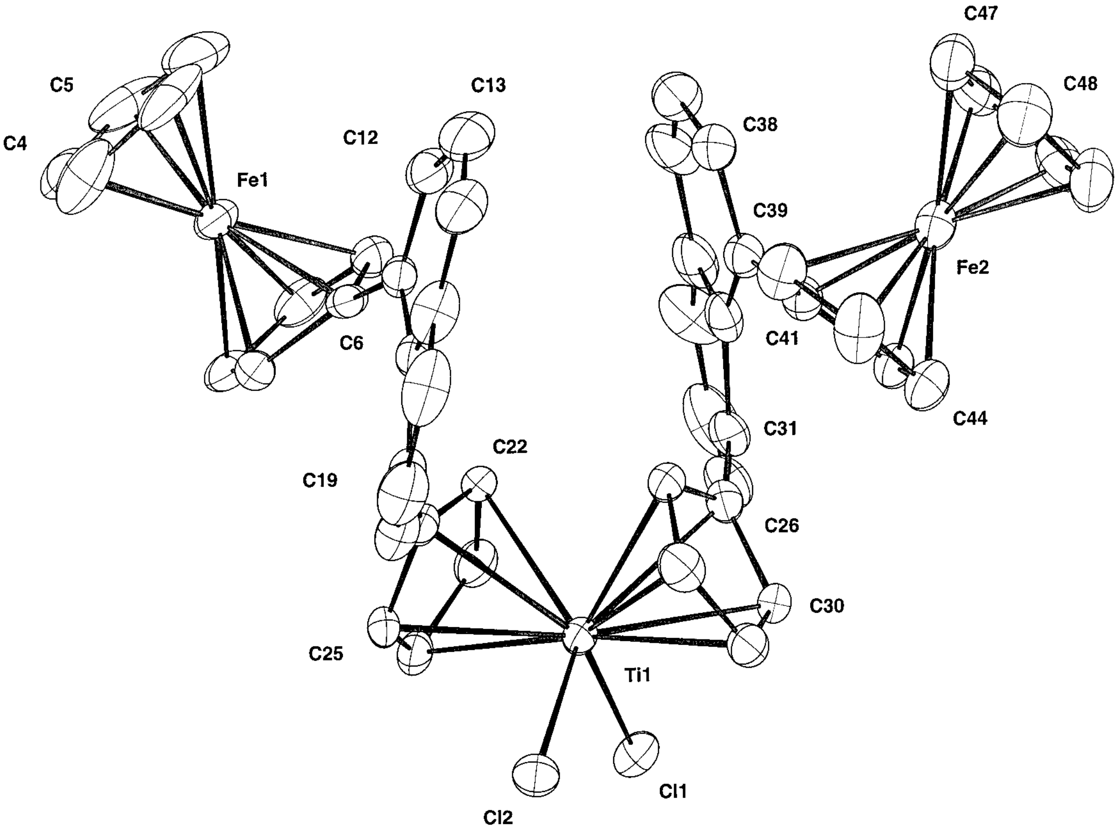

Figure 1. Molecular structure of **1c** (30% probability ellipsoids).

gave only mixtures of recovered starting material and ring-closure products **7a** and **7b.** These latter compounds are most likely formed by hydrolysis of the zirconium salt, either during the reaction or on workup, followed by protonation of the cyclopentadiene ring and intramolecular alkylation of the ferrocene nucleus in **5**.[16] Several attempts to prepare the zirconium complex using tetrakis(dimethylamino)zirconium, recently reported to give good yields of *ansa*-zirconium dihalides,[17] gave only recovered starting material, even after prolonged heating of the reaction solutions.

Initial attempts to prepare the titanium complex of **1c** using titanium tetrachloride met with a similar fate, and we finally turned to the use of titanium trichloride. This reactive salt has been used in the preparation of a number of highly hindered titanocene dichlorides.[18] Treatment of the lithium salt **6** with a suspension of titanium trichloride in THF, followed by reaction with HCl during workup, was found to give the desired titanium complex **1c** in moderate yield, together with smaller amounts of **7a** and **7b**. These reaction products were readily separated and purified by column chromatography on silica gel to give **1c** as a dark solid.

Black crystals suitable for X-ray crystallographic analysis were obtained by crystallization of the product from methylene chloride/hexane solutions by slow diffusion. The molecular structure of **1c** is shown in Figure 1; crystallographic data are given in Table 1.

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

chem formula	$C_{50}H_{38}Cl_2Fe_2Ti{\cdot}0.75CH_2Cl_2$
a, Å	10.571(2)
b, Å	15.227(2)
c, Å	15.605(3)
α, deg	79.57(1)
β, deg	74.86(2)
γ, deg	71.81(1)
V, Å^3	2290.1
Z	2
fw	933.054
space group	$P\bar{1}$ (C_i; No. 2)
T, °C	21(1)
λ, Å	0.710 73, graphite monochromator
ρ_{calcd}, g cm^{-3}	1.353
μ, mm^{-1}	1.03
abs cor	empirical, transmissn factors 0.838−1.00
data collection	$\pm h$, $-k$, $\pm l$ (to $2\theta = 24°$)
no. of rflns measd	7222; 6922 in unique set; 4048 with $I > 1.96\sigma(I)$; $R_{int} = 0.018$
R^a	0.0951
$R_w{}^a$	0.110

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

Selected bond distances in **1c** appear in Table 2; Fe−C distances are similar to those observed for **1a**, while Ti−C distances are slightly longer but again are similar to those found in Cp_2TiCl_2. The angle subtended at Ti by the centroids of the Cp moieties is 130.0°, which is near the average value (131.0°) found for Cp_2TiCl_2.[19] The longest distances are associated with the *ipso* C atoms of the Cp ligand, or the adjacent C atoms. The *ipso* C atoms of the Cp rings are displaced by +0.61 (C(6)), −0.67 (C(21)), +0.57 (C(26)), and −0.57 Å (C(41)) from the respective best planes of the naphthalene rings.

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Table 2. Selected Geometrical Parameters for 1c

(A) Bond Distances (Å)

Fe(1)−C(1)	2.034(13)	Fe(2)−C(47)	2.018(13)
Fe(1)−C(2)	2.033(12)	Fe(2)−C(48)	2.042(13)
Fe(1)−C(3)	2.043(14)	Fe(2)−C(49)	2.041(12)
Fe(1)−C(4)	2.000(12)	Fe(2)−C(50)	2.013(11)
Fe(1)−C(5)	2.003(13)	Ti(1)−Cl(1)	2.365(3)
Fe(1)−C(6)	2.085(8)	Ti(1)−Cl(2)	2.361(3)
Fe(1)−C(7)	2.034(9)	Ti(1)−C(21)	2.427(8)
Fe(1)−C(8)	2.027(9)	Ti(1)−C(22)	2.383(8)
Fe(1)−C(9)	2.030(10)	Ti(1)−C(23)	2.340(9)
Fe(1)−C(10)	2.039(9)	Ti(1)−C(24)	2.396(9)
Fe(2)−C(41)	2.073(9)	Ti(1)−C(25)	2.431(8)
Fe(2)−C(42)	2.047(11)	Ti(1)−C(26)	2.444(9)
Fe(2)−C(43)	2.036(12)	Ti(1)−C(27)	2.373(9)
Fe(2)−C(44)	2.028(11)	Ti(1)−C(28)	2.369(10)
Fe(2)−C(45)	2.037(10)	Ti(1)−C(29)	2.387(9)
Fe(2)−C(46)	2.037(13)	Ti(1)−C(30)	2.433(9)

(B) Interplanar Angles

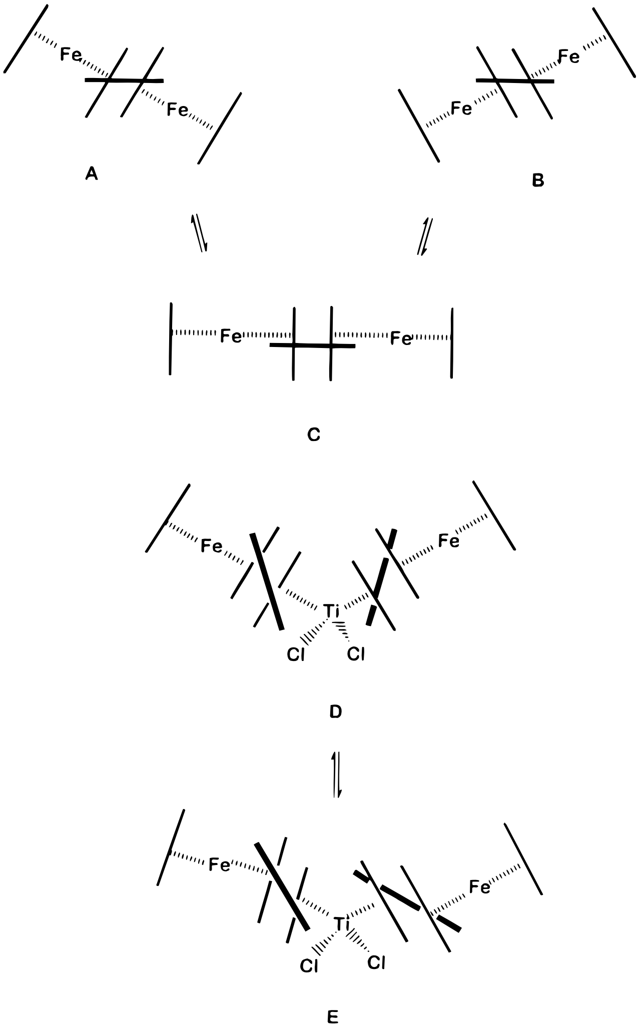
plane 1	plane 2	angle, deg	ϕ, deg
C(6)→C(10)	C(11)→C(20)	40.8	49.2
C(21)→C(25)	C(11)→C(20)	32.2	57.8
C(26)→C(30)	C(31)→C(40)	37.7	52.3
C(41)→C(45)	C(31)→C(40)	42.6	47.4
C(6)→C(10)	C(21)→C(25)	38.4	
C(26)→C(30)	C(41)→C(45)	34.6	
C(21)→C(25)	C(26)→C(30)	50.6	

[a] Rotation of Cp from 90° orientation to naphthalene.

These values, as well as the deviations of individual C atoms from the naphthalene best planes, are similar to the values previously observed.[2,18] Pertinent interplanar angles are also listed in Table 2.

It is of interest to note that molecular distortions associated with rotation of the Cp rings away from an orthogonal orientation to the naphthalene best planes (ψ) and Cp ring splaying, as measured by the interplanar angles (ϕ) between the pairs of *peri*-Cp rings, are considerably greater in **1c** than in **1a**. Thus, for **1c** $\psi = 47-58°$ and $\phi = 38-35°$, while for **1a** $\psi = 43-48°$ and $\phi = 23-28$.[2] We have earlier[20] provided evidence in support of the view that these molecular distortions are the result of electronic repulsions associated with the cofacial cyclopentadienyl rings. Thus, the distortions observed in **1a** are comparable to those found in the related dimetallic systems 1,8-diferrocenylnaphthalene (**8**;[21] $\psi = 45-47°$, $\phi = 29°$) and 1,8-diruthenocenylnaphthalene (**9**; $\psi = 42°$, $\phi = 26°$)[18] but are much decreased in the monocation $\mathbf{8}^+$ ($\psi = 29-31°$, $\phi = 17°$).[18] Theoretical analyses have shown[22] that there is significant electronic charge accumulation on the rings in ferrocene and that ionization leads to an electronic structure reorganization in which charge is effectively removed from the electron-rich rings in the neutral complex and transferred to the metal in the cation. Thus, the present results suggest that electronic charge on the Cp rings in **1c** and the resulting cofacial ring repulsions in this compound are significantly greater than in **1a**. The charge distribution in **1c** might be anticipated, since the electronegativity of the metal orbitals associated with metal−ring bonding in the titanium compound should be significantly lower than those in ferrocene.

Scheme 3



We note also that individual molecules in the racemic crystal adopt chiral conformations, with each molecule of **1c** containing a noncrystallographic C_2 axis which bisects the Cl−Ti−Cl angle. The alternative *meso* form of the molecules has a plane of symmetry which contains the $TiCl_2$ moiety. In solution, these isomers should be readily interconverted through a conformational change closely related to that illustrated in Scheme 3 for 1,8-diferrocenylnaphthalene.

For the latter compound, interconversion of its two mirror image forms **A** and **B** must take place through conformation **C**, in which the cofacial cyclopentadienyl rings are orthogonal to the average naphthalene ring. The barrier associated with this process has not been determined but is unlikely to be large. A similar rotation of one pair of cofacial Cp rings in **1c** shown in Scheme 3 serves to convert the chiral form of this compound **D** to its *meso* isomer **E**, while a similar rotation of the second pair of cofacial Cp rings interconverts **D** to its enantiomer.

Experimental Section

Preparation of 1-Cyclopentadienyl-8-iodonaphthalene (3). To a flame-dried 100 mL flask was added 20 mL of

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dry THF and freshly cracked cyclopentadiene (1.32 g, 20.0 mmol) under an argon atmosphere. The solution was cooled to 0 °C, and *n*-butyllithium (4.0 mL, 10.0 mmol of a 2.5 M solution in hexanes) was added by syringe. The mixture was stirred for 15 min at this temperature, and a solution of dry zinc chloride (2.72 g, 20 mmol) in THF (30 mL) was added via a cannula. The color of the solution lightened from pale yellow to almost colorless. The mixture was stirred for 1 h, after which time a faint white precipitate had formed. A solution of 8-diiodonaphthalene (1.90 g, 5.0 mmol) in THF (5 mL) was added by syringe, and the reaction mixture was stirred overnight at 0 °C. Analysis of the reaction mixture by TLC indicated that the transformation was complete, and the solution was poured into a separatory funnel charged with water (100 mL). The mixture was extracted with diethyl ether (3 × 50 mL), and the organic portions were combined before being dried over $MgSO_4$. The solution was filtered through a short plug of alumina on a 2 cm sintered-glass funnel with washing by diethyl ether, and the solvent was removed under reduced pressure. Column chromatography on silica gel with 2% diethyl ether/98% hexanes as the eluant afforded the title compound (1.42 g, 4.46 mmol) as a pale yellow oil (89%). This represents the average yield; other preparations led to yields between 80 and 95%. The product was obtained as an equimolar mixture of conjugated and cross-conjugated isomers in the ratio 1:1 (by NMR) and exhibited the same spectral characteristics as previously prepared samples.[5]

Preparation of 1-Ferrocenyl-8-iodonaphthalene (4). Freshly cracked cyclopentadiene (420 mg, 6.0 mmol) was added to a solution of 1-iodo-8-cyclopentadienylnaphthalene (450 mg, 1.4 mmol) in 15 mL of dry THF under an argon atmosphere. A slurry of $FePy_4(SCN)_2$ (3.4 g, 7.0 mmol) in THF was prepared from the salt, which had been washed with THF to remove ferric impurities. This was added to the reaction mixture by syringe through a wide-bore needle. The mixture was cooled to −78 °C, and potassium hexamethyldisilamide (14 mL, 7.0 mmol, 0.5 M solution in toluene) was added in one portion. The reaction mixture immediately became red, and the yellow suspension of $FePy_4(SCN)_2$ appeared to dissipate somewhat. The mixture was removed from the cooling bath, warmed to room temperature, and stirred for 30 min. The solution was then poured into a separating funnel containing water (50 mL), and this was extracted several times with 50 mL of diethyl ether. The combined organic portions were washed with water (2 × 50 mL) and brine (50 mL) and then dried over $MgSO_4$. Solvent was removed under reduced pressure to afford a red solid. This was purified by column chromatography on silica gel with 2% ether/98% hexanes as the eluant to afford the title compound as a red solid (227 mg, 37%), mp 192−194 °C. ^1H NMR (400 MHz, $CDCl_3$, COSY assignments): δ 8.39 (dd, 1H, J = 1.2, 7.3 Hz, ArH_7), 8.11 (dd, 1H, J = 1.2, 7.3 Hz, ArH_2), 7.81 (dd, 1H, J = 0.9, 8.3 Hz, ArH_4), 7.70 (dd, 1H, J = 1.2, 8.3 Hz, ArH_5), 7.47 (dd, 1H, J = 7.3, 8.3 Hz, ArH_6), 7.00 (dd, 1H, J = 7.3, 7.9 Hz, ArH_3), 4.59 (t, 2H, J = 1.8 Hz, CpH), 4.38 (t, 2H, J = 1.8 Hz, CpH), 4.10 (s, 5H, CpH). Anal. Calcd for $C_{20}H_{15}IFe$: C, 54.8; H, 3.4. Found: C, 54.7; H, 3.3. Also formed in the reaction was 1,1′-bis(8-iodo-1-naphthyl)ferrocene[3] (143 mg, 21%).

1-Cyclopentadienyl-8-ferrocenylnaphthalene (5). Method A. Cyclopentadienylzinc was prepared by the addition of *n*-butyllithium (0.8 mL, 2.0 mmol of a 2.5 M solution in hexanes) to a stirred solution of freshly cracked cyclopentadiene (150 mg, 2.27 mmol) dissolved in THF (20 mL) at 0 °C. Anhydrous zinc chloride (544 mg, 4.0 mmol) in THF (10 mL) was added, and after 1 h 1-iodo-8-ferrocenylnaphthalene (140 mg, 0.32 mmol) also in THF (5 mL) was introduced by syringe, followed by copper iodide (10 mg, 16 mol %). The solution was warmed to room temperature and stirred for 1 h, after which time analysis of the reaction mixture by TLC showed the reaction to be complete. The solution was diluted with diethyl ether (50 mL) and washed with a saturated aqueous solution of NH_4Cl. The organic portion was separated, dried over $MgSO_4$, and concentrated under vacuum. Purification of the residue by column chromatography on silica gel with 60% toluene/40% hexanes as the eluant afforded the title compound as a red solid (109 mg, 91%), as a 1:1.7 mixture of the two double-bond isomers A and B, respectively; mp 134−140 °C. IR (KBr): 3004, 1592, 1365, 1105, 1052, 1022, 1000, 952, 894, 824, 773, 672, 485 cm^{-1}. ^1H NMR (400 MHz, $CDCl_3$): δ 8.18 (d, 1H, J = 6.7 Hz, ArH_7 isomers A and B), 7.80 (dd, 0.6H, J = 2.4, 6.7 Hz, ArH_2 isomer B), 7.77 (dd, 0.4H, J = 2.4, 6.7 Hz, ArH_2 isomer A), 7.77 (d, 1H, J = 7.9 Hz, ArH_5 isomer A and B), 7.51 (t, 0.6H, J = 7.9, 7.9 Hz, ArH_6 isomer B), 7.50 (t, 0.4H, J = 7.9, 7.9 Hz, ArH_6 isomer A), 7.41 (m, 1.4H, ArH_3 isomers A and B and ArH_4 isomer A), 7.34 (d, 0.6H, J = 5.5 Hz, ArH_4 isomer B), 5.8−6.2 (m, 3H, CpH), 4.2 (bs, 0.4H, FcH_{α}, isomer A), 4.24 (bs, 0.6H, FcH_{α}, isomer B), 4.02 (bs, $0.6H_{\beta}$, FcH, isomer B), 3.97 (s, 5.4H, FcH_{β}, isomer A, FcH isomers A and B), 2.85 (bs, 1.2H, CpH isomer B), 2.74 (bs, 0.8H, CpH, isomer A). Anal. Calcd for $C_{25}H_{20}Fe$: C, 79.8; H, 5.4. Found: C, 79.6; H, 5.4.

Method B. Bromoferrocene[6] (1.5 g, 5.6 mmol) was dissolved in dry THF (10 mL) and cooled to −78 °C. BuLi (2.3 mL, 5.8 mmol) was added dropwise over 10 min, and the mixture was stirred for a further 1 h, after which time a heavy yellow precipitate had formed. The solution was warmed to room temperature and the solid dissolved, leaving an orange solution, which was stirred for 1 h. Zinc chloride (0.16 g, 4.15 mmol) was added as a solution in 8 mL of THF. The solution was stirred for a further 1 h, at the end of which time 1-iodo-8-cyclopentadienylnaphthalene (1.32 g, 4.15 mmol) and tetrakis(triphenylphosphine)palladium(0) (0.115 g, 2.5 mol %, 0.1 mmol) were mixed and added in THF (5 mL). The reaction mixture was stirred for 3 h, after which time no starting material remained (by TLC). The solution was poured into a separatory funnel charged with water (25 mL) and extracted with diethyl ether (2 × 50 mL). The combined organic extracts were washed with water (50 mL) and dried over $MgSO_4$ before being evaporated to dryness. The mixture was purified by column chromatography on basic alumina with an elution gradient of 100% hexanes (to remove the ferrocene) to 10% ether/90% hexanes. The product was obtained as an orange solid (1.18 g, 3.14 mmol) in 76% yield and exhibited the same spectral data as above.

Preparation of 1,1′-Bis(8-ferrocenyl-1-naphthyl)ferrocene (1a). The sodium salt **6** was formed by the addition of sodium bis(trimethylsilyl)amide (0.35 mL, 0.35 mmol, 1.0 M solution in THF) to a solution of **6** (125 mg, 0.33 mmol) in 10 mL of THF, cooled to 0 °C. The mixture was stirred for 1 h, and $FePy_4(SCN)_2$ (244 mg, 0.5 mmol) was added as a slurry in 5 mL of THF. The solution was warmed to room temperature and stirred for 2 h. Aqueous workup and extraction into hexanes (30 mL) followed by drying and subsequent filtration through a short pad of silica (4 cm in a 2 cm diameter sintered-glass funnel) provided, after removal of the solvent, a red solid. NMR of this material showed it to be the desired product **1a** in high purity (57 mg, 53%). The compound exhibited NMR spectral data identical with those previously reported.[10] ^1H NMR (400 MHz, $CDCl_3$): δ 8.01 (d, 2H, J = 7.0 Hz, ArH_7), 7.68 (d, 2H, J = 7.9 Hz, ArH_2), 7.60 (d, 2H, J = 7.5 Hz, ArH_5), 7.58 (bs, 2H, ArH_4), 7.41 (t, 2H, J = 7.3, 7.3 Hz, ArH_3), 7.05 (t, 2H, J = 7.6, 7.6 Hz, ArH_6), 4.02 (bs, 4H, CpH_{α}), 3.80 (s, 14H, $CpH_{\text{terminal,}}$ CpH_{α}), 3.77 (s, 4H, CpH_{β}). 3.55 (s, 4H, CpH_{β}).

Preparation of 1,1′-Bis(8-ferrocenyl-1-naphthyl)cobaltocenium Salts (1b). The anion **6** was prepared as above in the same quantity. $CoBr_2$ was added as a solid in one portion, and the solution immediately became black. The mixture was stirred for a further 1 h, and the appropriate acid was added in order to form the cobaltocenium species. After 1 h at room temperature the mixture was diluted with methylene chloride (10 mL) and washed with water (2 × 50 mL). The salt was precipitated from the organic portion by the addition of diethyl ether (100 mL), and the solid material was collected by filtration. This was taken up again into methylene chloride (10 mL) and reprecipitated to afford the salt **3b** as a brown solid which resisted all attempts at crystallization. IR (KBr): 3110, 1478, 1185, 1134, 1006, 1070, 1035, 1002, 8, 770, 558, 484 cm^{-1}. ^1H NMR (400 MHz, $CDCl_3$): 8.10 (d, 2H, J = 6.4 Hz, ArH_7), 7.80 (d, 2H, J = 7.9 Hz, ArH_2), 7.77 (d, 2H, J = 7.9 Hz, ArH_5), 7.57 (t, 2H, J = 7.3, 7.3 Hz, ArH_3), 7.13 (d, 2H, J = 7.0 Hz, ArH_4), 6.82 (t, 2H, J = 7.6, 7.6 Hz, ArH_6), 5.16 (bs, 4H, CoCpH), 5.00 (bs, 4H, CoCpH), 4.04 (s, 4H, FeCpH), 3.91 (bs, 4H, FeCpH). 3.89 (s, 10H, FcCpH). ^{13}C NMR (100.5 MHz, $CDCl_3$): 135.6, 134.9, 132.7, 132.3, 131.9, 130.6, 127.6, 126.6, 125.7, 124.4, 109.5, 91.6, 84.4, 81.8, 71.5, 70.1, 68.1. Anal. Calcd for $C_{50}H_{38}Fe_2CoPF_6\cdot{}^1/_2CH_2Cl_2$: C, 60.83; H, 3.94. Found: C, 60.58; H, 3.80.

Preparation of 1,1′-Bis(8-ferrocenyl-1-naphthyl) titanocene dichloride (1c). The anion **6** was formed by the addition of *n*-BuLi (0.2 mL, 0.5 mmol, 2.5 M solution in hexanes) to a solution of **5** (195 mg, 0.52 mmol) in 10 mL of THF, cooled to 0 °C. The solution was stirred for 2 h and then cooled to −78 °C, and $TiCl_3$ was added dropwise as a suspension in 5 mL of THF. The mixture was warmed to room temperature and was stirred for a further 4 h.

The mixture was poured into a separatory funnel containing concentrated HCl (5 mL) and extracted with methylene chloride (2 × 10 mL). The extracts were combined and washed with water (2 × 20 mL) before being dried with $MgSO_4$. Removal of solvent left a dark red solid. This was purified by column chromatography on silica gel with 30% ether/70% hexanes as eluant, affording the title compound **1c** as a very dark solid (93 mg, 42%). An equimolar (by NMR) mixture of **7a** and **7b** (57 mg, 29%) eluted before **1c** and was further separable by preparative TLC to afford the two isomeric compounds as red solids. The titanium compound was crystallized from methylene chloride by allowing hexanes to diffuse slowly into the solution at room temperature. An X-ray structure determination was carried out on the black crystals. Mp: >360 °C. IR (KBr): 3092, 1589, 1412, 1389, 1184, 1134, 1106, 1045, 1026, 1001, 825, 770, 693 cm^{-1}. ^1H NMR (400 MHz, $CDCl_3$): δ 7.89 (d, 2H, J = 8.0 Hz, ArH_7), 7.82 (d, 2H, J = 8.0 Hz, ArH_2), 7.68 (d, 2H, J = 7.0 Hz, ArH_5), 7.58 (t, 2H, J = 7.6, 7.6 Hz, ArH_3), 7.36 (t, 2H, J = 7.3, 7.3 Hz, ArH_6), 7.26 (d, 2H, J = 7.0 Hz, ArH_4), 5.49 (s, 4H, TiCp), 5.38 (s, 4H, TiCp), 3.78 (s, 10H, FcCp), 3.70 (s, 4H, FeCp), 3.61 (s, 4H, FeCp). ^{13}C NMR (100.5 MHz, $CDCl_3$): δ 136.0, 135.0, 132.1, 131.4, 130.7, 130.2, 130.1, 129.0, 127.0, 125.5, 124.9, 124.6, 118.8, 90.3, 70.5, 69.9, 7.3. Anal. Calcd for $C_{50}H_{38}Fe_2TiCl_2$: C, 69.07; H, 4.40. Found: C, 68.49; H, 4.94.

Compound 7a. Mp: 142−144 °C. IR (KBr): 3045, 2919, 2851, 1591, 1508, 1361, 1323, 1297, 1189, 1108, 1034, 1001, 817, 800, 778, 541, 496, 486, 468 cm^{-1}. ^1H NMR (400 MHz, $CDCl_3$): δ 7.70 (dd, 1H, J = 7.9, 1.8 Hz, ArH_7), 7.65 (d, 1H, J = 7.9 Hz, ArH_2), 7.44−7.52 (m, 3H, $ArH_{3,4,5}$), 7.35 (dd, 1H, J = 7.9, 7.9 Hz, ArH_6), 6.24 (m, 1H, vinyl-H), 6.14 (m, 1H, vinyl-H), 4.89 (d, 1H, J = 1.2 Hz, FcH), 4.28 (dd, 1H, J = 1.8, 2.4 Hz, FcH), 4.23 (d, 1H, J = 1.2 Hz, FcH), 3.73 (s, 5H, FcH), 2.50 (m, 2H, CH_2), 2.07 (ddd, 1H, J = 12.2, 8.0, 4.3 Hz, C*H*H), 1.97 (ddd, 1H, J = 15.3 12.2, 9.2 Hz, CH*H*). ^{13}C NMR (100.5 MHz, $CDCl_3$): δ 143.2, 137.6, 134.1, 134.09, 132.8, 127.4, 126.5, 126.4, 126.0, 125.8, 124.2, 118.1, 92.6, 70.4, 70.3, 68.1, 66.0, 62.9, 54.8, 48.6, 32.0.

Compound 7b. Mp: 137−140 °C. IR (KBr): 3052, 2696, 2852, 1592, 1508, 1362, 1106, 1036, 1000, 830, 820, 774, 760, 738, 621, 542, 496, 485 cm^{-1}. ^1H NMR (400 MHz, $CDCl_3$): δ 7.67 (dd, 1H, J = 7.9, 1.2 Hz, ArH_7), 7.64 (dd, 1H, J = 7.9, 1.2 Hz, ArH_2), 7.44−7.52 (m, 3H, $ArH_{3,4,5}$), 7.35 (dd, 1H, J = 7.3, 8.6 Hz, ArH_6), 5.52 (m, 2H, vinyl-H), 4.87 (dd, 1H, J = 2.4, 1.2 Hz, FcH), 4.34 (d, 1H, J = 2.4 Hz, FcH), 4.30 (d, 1H, J = 2.2 Hz, FcH), 3.84 (s, 5H, FcH), 3.20, (m, 1H, C*H*H), 2.8−3.0 (m, 3H, CH_2, CH*H*). ^{13}C NMR (100.5 MHz, $CDCl_3$): δ 144.3, 143.5, 133.9, 133.8, 127.0, 126.6, 126.5, 126.0, 124.94, 124.93, 118.3, 94.6, 78.7, 70.4, 70.3, 68.5, 66.8, 62.2, 54.7, 43.4, 33.9.

X-ray Structure Determination of 12b, $C_{50}H_{38}Cl_2Fe_2Ti\cdot 0.75CH_2Cl_2$. Crystallographic data for compound **1c** are summarized in Table 1. Data were collected on a Nonius CAD-4 Turbo diffractometer (Mo Kα radiation, λ = 0.710 73 Å).[23] Data were processed using the Nonius MolEN package;[24] the structure was solved by direct methods (SIR-92).[25] Full-matrix least-squares refinement was carried out using the Oxford University CRYSTALS-PC system.[26] All non-hydrogen atoms were refined using anisotropic displacement parameters. H atoms were fixed at calculated positions, which were updated following each least-squares cycle. Solution of the structure was complicated by the presence of disordered dichloromethane, with partial occupancy at multiple locations. The final model contains 0.75 CH_2Cl_2 at two sites, but the poor crystal quality limited this part of the structure solution. Inability to determine a precise solution for the disordered solvent led to the relatively high R value of 0.095. However, the organometallic moiety is not disordered, and geometric information derived therefrom will be useful within the limit of the quoted errors. Drawings were produced using the Oxford University program CAMERON.[27] A full report on the structure is available as a CIF file.

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Supporting Information Available: X-ray crystallographic files, in the CIF format, for structure **12b**. This material is available free of charge via the Internet at http://pubs.acs.org.

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