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Synthesis of New Biferrocene Derivatives Containing Interannular Bridges and Their Mixed-Valence Analogues

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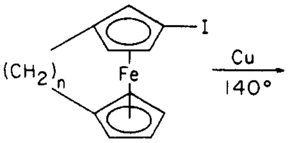
A series of biferrocene (Fc-Fc) (**1**) related compounds consisting of the coupled bridged ferrocenes [3]Fc-Fc (**2**), [3]Fc-[3]Fc (**3**), [4]Fc-Fc (**4**), [4]Fc-[4]Fc (**6**), and [4]Fc-[3]Fc (**5**) (Fc = ferrocene and [*n*]Fc = [*n*]-ferrocenophane) has been synthesized, and intervalence electron transfer in their mixed-valence cations has been investigated. The dimers **3** and **6** are prepared by Ullmann coupling of 3-I-[3]Fc (**11**) and 3-I-[4]Fc (**12**), respectively. The unsymmetrical compounds **2** and **4** are synthesized by the cross-coupling of the above iodo derivatives with ferrocenylzinc chloride using $PdCl_2(dppf)$ as catalyst. The same catalyst is used to couple **12** with 3-ZnCl-[3]Fc to give **5**. Synthesis of the iodo precursors **11** and **12** is also described. Cyclic voltammetry of compounds **1**–**6** in CH_3CN shows two reversible one-electron processes for each of the coupled compounds. Mixed-valence ions of **1**–**6** are prepared by controlled current oxidation, and the intervalence-transfer bands in the near-IR are reported.

Introduction

The use of mixed-valence organometallics has enabled systematic and creative investigation into the factors that influence intramolecular electron transfer. Using the parent mixed-valence systems of biferrocene (**1**)[1,2] and the Creutz–Taube ion,[3] synthetic modification has allowed study of the effects of distance between subunits,[4,5] saturated and unsaturated linking groups,[6-11] inequivalent subunits,[12,13] and different degrees of subunit interaction.[14-16] Much of what has been learned from the study of mixed-valence chemistry can be applied to the understanding of intramolecular electron transfer in more elaborate inorganic and biological systems.[17-19]

By utilizing the synthetic versatility afforded by the ferrocene moiety, we have developed a series of new mixed-valence biferrocene derivatives containing synthetically built-in symmetry distortions in order to investigate the effect that differences in the symmetry of the subunits have on the properties of the intervalence transfer transition. We report here on the synthesis of compounds **2**–**6** (Figure 1) and their mixed-valence ions.

Scheme I



3 (n=3)
6 (n=4)

Compounds **1**–**6** appear in Figure 1 along with the abbreviated names, derived from the subunits, used in this paper. The three-carbon-bridged ferrocene **7** has been referred to in the literature as 1,1′-trimethyleneferrocene[20] and under the cyclophane system as [3]ferrocenophane,[21,22] and will be referred to here as [3]Fc. A similar approach is taken in the two- and four-carbon bridged ferrocenes [2]Fc (**8**) and [4]Fc (**9**), respectively. A bridge between the rings of ferrocene of three atoms or less bends the ferrocene molecule such that the planes of the rings are no longer parallel. Although the crystal structure for [3]-ferrocenophane (**7**) is not known, a crystal structure of α-keto[3]ferrocenophane[23] (**10**) shows that the dihedral angle defined by the planes of the two cyclopentadienyl rings is about 9°. In the two-carbon-bridged 1,1′-tetramethylethyleneferrocene,[24] the angle of distortion is 23°. The shortest alkyl bridge that does not bend the ferrocenyl unit is a four-carbon bridge.

In the mixed-valence systems where there exist some degree of electronic interaction between the subunits, a new electronic transition is found in the visible to near-IR region of the spectrum that is attributable to intervalence electron transfer (eq 1). Of the theoretical models de-

$$X^MY^N \xrightarrow{h\nu} X^{M+1}Y^{N-1} \qquad (1)$$

veloped to describe the properties of mixed-valence sys-

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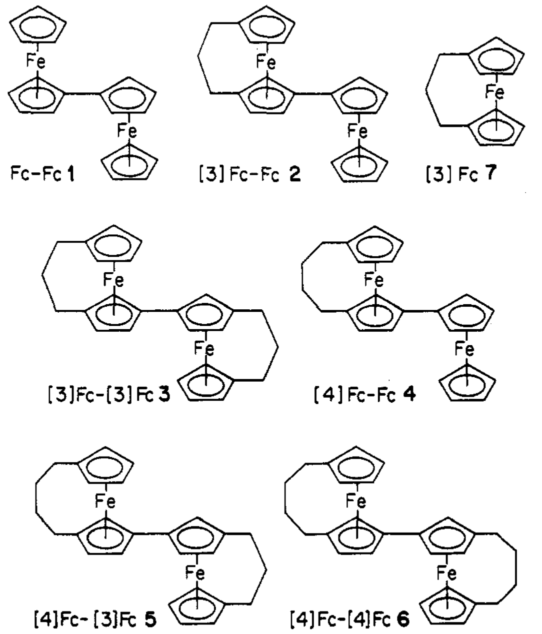


Figure 1. Structures and abbreviated names for compounds 1–7.

tems, including the intervalence transition, the simple model first proposed by Hush[25] is probably most widely utilized. In this model, the initial and final states are depicted as two weakly interacting potential surfaces separated on a configurational coordinate. For the symmetrical case (X = Y in eq 1), the energy of the intervalence transition, E_{op}, corresponds to a Franck–Condon transition from the ground level of the initial state to a vibrationally excited final state. Treating the intervalence transfer band as the totality of Franck–Condon transitions from populated levels of the initial state to the final state, in the high-temperature limit the Hush formulas result

$$E_{op}/E_{th} = 4 \tag{2}$$

$$(\Delta\nu_{1/2})^2 = 16kT \ln 2\bar{\nu}_{max} \tag{3}$$

where E_{th} is the energy barrier to thermal electron transfer and $\bar{\nu}_{max}$ and $\Delta\bar{\nu}_{1/2}$ are the band maximum and half-width of the intervalence transfer band, respectively.

For the unsymmetrical case (X $\neq$ Y), the potential surfaces are vertically displaced by an amount E_0 corresponding to the difference in ground-state energy of the two valence states. In this case, eq 2 and 3 become

$$E_{th} = (E_{op})^2/4(E_{op} - E_0) \tag{4}$$

$$(\Delta\bar{\nu}_{1/2})^2 = 16kT \ln 2(\bar{\nu}_{max} - \bar{\nu}_0) \tag{5}$$

Results and Discussion

Compounds 2–6 were synthesized from the corresponding subunits employing two different coupling schemes. Biferrocene[26] and bis(fulvalene)diiron[14] (BFD) have been prepared by Ullmann coupling of iodoferrocene and 1,1′-diiodoferrocene, respectively. While this procedure is not useful for cross-coupling reactions, it is an extremely simple and efficient route to symmetrically coupled biferrocenes. The dimers [3]Fc-[3]Fc and [4]Fc-[4]Fc were prepared in this manner (Scheme I). The yield of [3]Fc-[3]Fc is quantitative, but as 3-iodo-[4]ferrocenophane is difficult to purify, the yield of [4]Fc-[4]Fc is somewhat lower (85–93%), probably due to the presence of some diiodo derivatives in the starting material.

The use of palladium and nickel catalysts in cross-coupling reactions of various organometallics with organic halides has received much recent attention[27] (Scheme II).

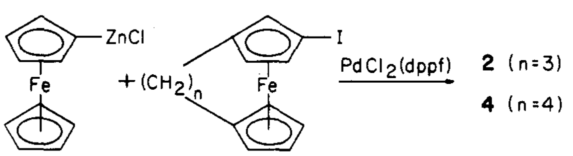
Scheme II

$$\text{R–m} + \text{R}'\text{–X} \xrightarrow{\text{ML}_n} \text{R–R}' + \text{mX}$$

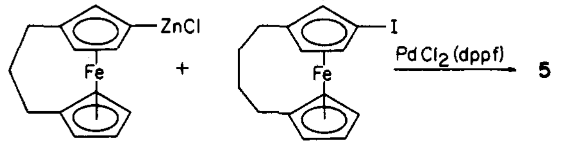
$$\text{M} = \text{Ni, Pd; m} = \text{Li, Mg, Zn, Al; X} = \text{Cl, Br, I}$$

Although different choices of M, m, and X have been successful depending upon the application, it seems that the use of organozinc reagents with the catalyst dichloro[1,1′-bis(diphenylphosphino)ferrocene]palladium(II) ($PdCl_2$(dppf)) generally gives high yields of coupled material with low incidence of metal–halogen exchange and cross-homo scrambling.[28] It was this approach that was used for the cross-coupling reactions here. Ferrocenylzinc chloride was coupled with the corresponding 3-iodo[*n*]ferrocenophane to give [3]Fc-Fc (50%) and [4]Fc-Fc (48%) (Scheme III). In an analogous fashion, [3]Fc-[4]Fc (32%) was obtained (Scheme IV). Indeed, these reagents result in less than 10% metal–halogen exchange and allow the recovery of the more difficult to prepare substituted ferrocenyl halide. Coupling involving iodo derivatives is more facile than with the corresponding bromo derivatives, although generally they are more difficult to purify. Where metalation is required (Schemes III and IV), the zinc chloride adducts were prepared by lithium–bromine exchange followed by reaction with $ZnCl_2$ (Scheme V). These reaction solutions were used directly in the coupling reactions. It is necessary to remove any alkyl halide formed upon metal–halogen exchange. In the case of ferrocene, ferrocenyllithium precipitates out of hexane, allowing the solution containing the alkyl halide to be decanted. Where *n* = 3 (Scheme V), however, [3]FcLi does not precipitate, and the alkyl halide was eliminated by employing 2 equiv of *t*-BuLi where the second equivalent reacts with the *tert*-butyl bromide to form isobutane and isobutylene.

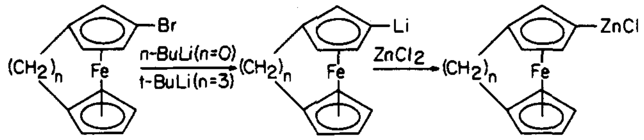
Scheme III



Scheme IV



Scheme V



Useful quantities of the 3-halo[*n*]ferrocenophanes 11–13 were prepared from the mercuric chloride derivatives in analogy to the method of Rosenblum[29] for the preparation

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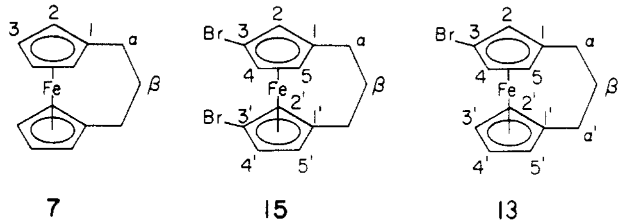
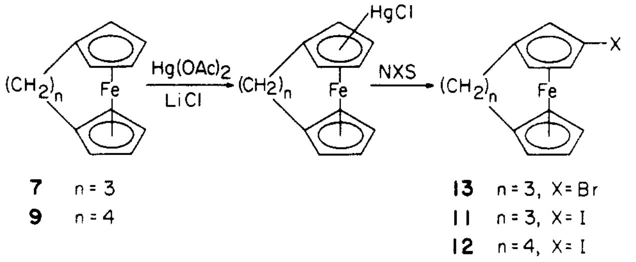


7 15 13

Figure 2. Carbon-labeling scheme for ^{13}C NMR analysis.

Scheme VI



Scheme VII

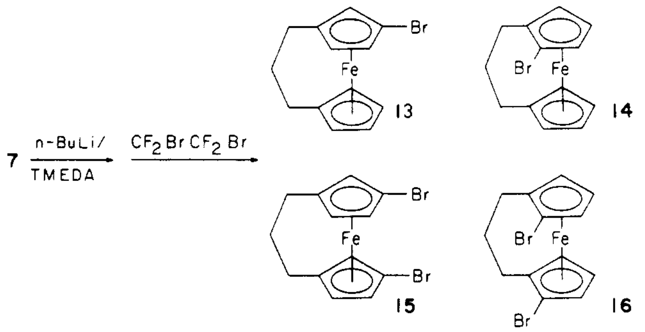


Table I. ^{13}C NMR of Dibromo[3]ferrocenophanes

compd	δ	^{1}H-decoupled assignt	coupled spectrum	
[3]Fc	24.5	Cα	t	^1J = 126 Hz
	35.1	Cβ	t	^1J = 127 Hz
	68.2	C3	d of q	^1J = 175 Hz, ^2J = 6 Hz
	69.4	C2	d of m	^1J = 170 Hz
	85.5	C1	br s	
3,3′-dibromo[3]-Fc	23.9	Cα	t	^1J = 127 Hz
	35.1	Cβ	t	^1J = 127 Hz
	69.2	C5	d of m	^1J = 176 Hz
	71.7	C2	d of t	^1J = 182 Hz, ^2J = 6 Hz
	72.3	C4	d of m	^1J = 176 Hz
	79.7	C3	m	
	85.7	C1	m	
2,2′-dibromo[3]-Fc	21.8	Cα	t	^1J = 125 Hz
	34.4	Cβ	t	^1J = 126 Hz
	67.4	C4	d of t	^1J = 178 Hz, ^2J = 6 Hz
	67.7	C5	d of m	^1J = 175 Hz
	72.1	C3	d of t	^1J = 182 Hz, ^2J = 6 Hz
	81.6	C2	m	
	86.1	C1	m	

of haloferrocenes. Due to the presence of the alkyl bridge, a mixture of monosubstituted and disubstituted isomers results upon mercuration which is difficult to separate. By proceeding with the halogenation, isolation of the 3-halo derivatives becomes manageable by column chromatography. Thus, 3-bromo[3]ferrocenophane (**13**), 3-iodo[3]-ferrocenophane (**11**), and 3-iodo[4]ferrocenophane (**12**) were prepared in 50%, 45%, and 31% yields, respectively (Scheme VI).

Lithiation and subsequent halogenation of [3]-ferrocenophane (**7**) has previously been reported by Hillman,[30] using n-BuLi/TMEDA to give a mixture of mono- and disubstituted compounds (Scheme VII). While reasonable structural assignments of these compounds were given on the basis of ^{1}H NMR data, a more detailed characterization was thought necessary. In addition, although usable quantities of monohalo derivatives **11**–**13** are not obtainable via this route, isolation of known samples would help in the characterization of these materials when synthesized by alternative methods.

Structural assignments of the two dibromo[3]-ferrocenophanes (**15** and **16**) are nicely confirmed by comparison of their ^{13}C NMR spectra to that of unsubstituted [3]ferrocenophane (Table I; see Figure 2 for labeling schemes). In the ^{1}H-decoupled spectrum of [3]Fc, absorptions due to the trimethylene bridge, Cα and Cβ, are at δ 22.5 and 35.1, respectively. The quaternary C1 is seen at δ 85.5, and the remaining two ring carbons are at δ 68.2 (C3) and 69.4 (C2). The latter two assignments are made on the basis of the proton-coupled spectrum where the C3 resonance is split into a doublet of quartets (^1J = 175 Hz, ^2J = 6 Hz) and the C2 resonance is split into a doublet of multiplets (^1J = 170 Hz). The increased complication in the C2 resonance is due to splitting by methylene protons of the bridge. This was confirmed by single frequency decoupling of the methylene protons that collapsed the doublet of multiplets into a doublet of quartets. In the dibromo derivatives, bromine substitution shifts the substituted carbon downfield by 10 ppm and the carbon α to substitution downfield by 3–5 ppm. On the basis of the number of carbons shifted and the multiplicity of splitting in the proton-coupled spectra (Table I), the assignments of compounds **15** and **16** as 3,3′-dibromo- and 2,2′-dibromo[3]ferrocenophane, respectively, were confirmed.

Proton-decoupled spectra of the monobromo compounds **13** and **14** (see analytical data in Experimental Section) show that in 3-Br-[3]Fc, as for [3]Fc and the dibromo compounds, the bridge carbons give two resonances in the ratio of 2:1 for Cα and Cβ. In the 2-bromo derivative, however, C2 substitution influences the trimethylene bridge, causing an inequality of Cα and Cα', and three signals are seen in this region. This is consistent with the increased distortion of the signal due to the trimethylene bridge in the 2-substituted compounds seen in the ^{1}H NMR (see below).

Due to the fluxional nature of the bridge in [3]Fc, only a broad singlet is observed in the ^{1}H NMR for the methylene bridge protons at room temperature. In all of the bromine-substituted compounds, the trimethylene bridge absorption becomes more complicated. Deformation of the bridge in the 2-substituted and the 2,2′-disubstituted compounds, as noted by Hillman, causes this resonance to be split by more than 0.3 ppm. This large splitting of the methylene proton resonance in 2-substituted ferrocenophanes is extended to the iodo derivatives and thus allows differentiation between the different monosubstituted compounds.

It should be noted that in the coupled compounds **3**, **5**, and **6**, where each subunit contains an intramolecular bridge, a mixture of diasteromers exists. The presence of diastereomers has apparently not manifested itself in any of the physical properties discussed here, although this may account for why these materials have a particularly broad melting range (see Experimental Section) and also why the solids do not seem to form in a singly crystalline manner.

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Table II. Cyclic Voltammetry 0.1M $TBABF_4/CH_3CN$ vs. $Ag/AgNO_3$

compd[c]	$E_{1/2}(1)$[a] Ag/Ag$^+$	$E_{1/2}(1)$ Fc/Fc$^+$	$(E_{pa} - E_{pc})$[b]	$E_{1/2}(2)$ Ag/Ag$^+$	$E_{1/2}(2)$ Fc/Fc$^+$	$(E_{pa} - E_{pc})$	$\Delta E_{1/2}(2 - 1)$
ferrocene	0.070	0.000	69				
biferrocene	−0.010	−0.080	72	0.305	0.235	70	315
[4]Fc-Fc	−0.071	−0.141	75	0.272	0.202	65	343
[3]Fc-Fc	−0.108	−0.178	70	0.264	0.194	75	372
[4]Fc-[3]Fc	−0.116	−0.186	70	0.229	0.159	65	345
[4]Fc-[4]Fc	−0.125	−0.195	76	0.184	0.114	79	309
[3]Fc-[3]Fc	−0.144	−0.214	70	0.245	0.175	74	389

[a] Average of three scan speeds: 200, 100, and 50 mV/s. [b] 100-mV/s sweep. [c] All concentrations equal 1 mg/10 mL.

Table III. Near-IR Data[a] on Mixed-Valence Derivatives

compd	$\bar{\nu}_{max}$, cm^{-1} (ϵ, M^{-1} cm^{-1})	$\Delta\bar{\nu}_{1/2}$(obsd), cm^{-1}	$\Delta\bar{\nu}_{1/2}$(calcd), cm^{-1}
(Fc-Fc)$^+$	5500 (410)	4400	3560
([3]Fc-Fc)$^+$	5850 (750)	4000	3520
([4]Fc-Fc)$^+$	5680 (620)	4300	3400
([3]Fc-[4]Fc)$^+$	5500 (1000)	3400	3470
([3]Fc-[3]Fc)$^+$	5520 (1470)	2900	3570
([4]Fc-[4]Fc)$^+$	5210 (970)	3800	3470

[a] CH_3CN solutions containing 0.1 M $TBABF_4$.

Cyclic voltammetry data in CH_3CN for compounds 1–6 are listed in Table II. Potentials are referenced to Ag/$AgNO_3$ and also to the ferrocene/ferrocenium couple. In CH_3CN all of the coupled materials show two reversible single-electron waves, with the difference in oxidative and reductive peak potentials ($E_{pa} - E_{pc}$) approaching the theoretical limit of 60 mV for a reversible one-electron process. For all compounds, a 1:1 relationship of the anodic and cathodic peak currents was demonstrated.

In the series of coupled compounds Fc-Fc, [3]Fc-Fc, and [4]Fc-Fc, the effect of ferrocene as a substituent is as an electron donor and, therefore, the oxidation potentials of these derivatives are lower than that of ferrocene itself. The effect of alkyl substitution is to lower the oxidation potentials relative to biferrocene. The difference in half-wave potentials between the first and second oxidations ($\Delta E_{1/2}$) is an indication as to the extent of electronic interaction between the subunits when considering a series of closely related compounds. The largest $\Delta E_{1/2}$ values are found in the [3]Fc-[3]Fc and [3]Fc-Fc derivatives, suggesting a higher degree of interaction in these compounds than in the other coupled products. The smallest $\Delta E_{1/2}$ are found for Fc-Fc and [4]Fc-[4]Fc.

Electronic absorption spectroscopy shows that there is a new transition in the near-IR of the mixed-valence derivatives that, as is the case for biferrocene, can be assigned to the intervalence transfer transition. Solutions of the mixed-valence derivatives of compounds 1–6 were prepared by controlled current oxidation. The positions and intensities of these bands along with the width at half-maximum ($\Delta\bar{\nu}_{1/2}$) are listed in Table III. Also listed are the calculated values of $\Delta\bar{\nu}_{1/2}$ based on eq 3 and 5 as predicted by the Hush model (see Introduction).[31]

Comparison of the calculated values for $\Delta\bar{\nu}_{1/2}$ to the observed values shows that generally the observed bandwidths are wider than the values predicted by the model. This is not unreasonable considering the assumptions on which eq 3 and 5 are based. Values for the ratio $\Delta\bar{\nu}_{1/2}$(obsd)/$\Delta\bar{\nu}_{1/2}$(calcd) of 1.1:1.3 have previously been found for mixed-valence biferrocene in a variety of solvents.[5] In exception to this are the cases of ([3]Fc-[3]Fc)$^+$ and ([4]Fc-[3]Fc)$^+$ where the bands are sharper than predicted by the Hush treatment with $\Delta\bar{\nu}_{1/2}$(obsd)/$\Delta\bar{\nu}_{1/2}$(calcd) about 0.8 for ([3]Fc-[3]Fc)$^+$ and 0.95 for ([4]Fc-[3]Fc)$^+$. These bands are also sharper and more intense than any other IT bands in the series. Along with the electrochemical results, this could imply a stronger interaction in these compounds—outside the "weak interaction" criterion of the Hush model. Further work is underway to fully characterize the differences in electronic interactions in these mixed-valence systems and to investigate the effects that these differences have on intervalence transfer including spin resonance and Mössbauer studies.

Experimental Section

General Data. Infrared spectra were recorded on a Perkin-Elmer 339B spectrophotometer; ^1H NMR were obtained either on a Varian CFT-20 (80-MHz) or Varian XL-400 (400-MHz) spectrometer with tetramethylsilane as an internal standard. ^{13}C NMR (100 MHz) were run on the Varian XL-400. Near-IR spectra were run on a Perkin-Elmer Lambda-9 spectrophotometer. Low-resolution mass spectra were obtained on a KRATOS MS-50 mass spectrometer (at The Middle Atlantic Mass Spectrometry Laboratory, The Johns Hopkins University School of Medicine). High-resolution mass spectra were obtained from the Mass Spectrometry Facility at Cornell University employing an AEI-MS-902. Elemental analysis was performed by Galbraith Laboratories, Inc., Knoxville, TN. In the experimental procedures described below, "short-path" liquid chromatography refers to a technique where TLC grade (EM Science) silica gel is used with an air-pressure-driven column similar to that described for flash chromatography.[32]

Electrochemistry. Cyclic voltammograms were obtained by using a PAR 175 universal programmer as a sweep generator and a PAR 173 potentiostat for potential control. Preparative oxidations employed a PAR 179 digital coulometer. A standard three-electrode configuration was used consisting of a platinum button (Beckman) working electrode, a silver or nickel counter electrode, and either a saturated calomel (SCE) or silver–silver nitrate ($Ag/AgNO_3$) reference electrode. The reference electrode was connected to the electrolysis compartment via a salt bridge that contained the electrolytic solution. Solvents for electrochemical studies were dried by passing through a column of activated neutral alumina and stored under argon. Tetrabutylammonium tetrafluoroborate (n-Bu_4NBF_4) was purchased from Southwestern Analytical Chemicals, Inc., Austin, TX, and was used without further purification. Monocations of compounds 1–6 for electronic spectroscopy were prepared by controlled current oxidation. Samples for absorption spectra were transferred via syringe to a septum-sealed quartz cell.

Materials. Reagent grade hexanes for synthesis was washed with H_2SO_4/HNO_3 followed by H_2O, bubbled with argon, predried over Na_2SO_4, distilled from CaH_2, and stored under argon. DMF was vacuum distilled from BaO and stored under argon. Reagent grade methylene chloride was used without further purification. Dichloro[1,1′-bis(diphenylphosphino)ferrocene]palladium(II) ($PdCl_2$(dppf)) was purchased from Alfa Products and used as received. All reactions were run under argon.

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[31] The difference in ground-state energy of the two valence isomers, $\bar{\nu}_0$, in the unsymmetrical compounds is not directly measurable. As the subunits are electronically very similar, $\bar{\nu}_0$ was estimated from the difference in redox potentials of the subunits themselves. Talham, D. R.; Cowan, D. O., unpublished results.

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α-Keto[3]ferrocenophane (**10**) was synthesized by the procedure of Watts.[33] [3]Ferrocenophane (**7**) was prepared by mixed hydride reduction of the α-ketone as per the procedure of Rinehart.[20] [4]Ferrocenophane (**9**) was obtained by a modified Wolff–Kishner reduction of β-keto[4]ferrocenophane by the procedure of Rosenblum,[34] although the reaction temperatures cited caused extensive decomposition. Optimum yields (90%) resulted if the reaction temperature was kept between 190 and 200 °C: mp 62–63 °C (lit. mp 63–64 °C). β-Keto[4]ferrocenophane was prepared by diazomethane bridge enlargement of α-keto[3]ferrocenophane by a slight modification of the published procedure.[34] Increased yields (84%) were obtained by distilling the ethereal diazomethane solution directly into a stirred solution of the starting ketone.

Lithiation of [3]Ferrocenophane with Subsequent Bromination by Dibromotetrafluoroethane. The procedure of Hillman[30] was used with a modification in the isolation. In a 250-mL, three-neck, round-bottom flask equipped with stir bar, condenser, and dropping funnel was placed 1.0 g (4.4 mmol) of [3]ferrocenophane in 30 mL of dry hexanes. *n*-BuLi (11 mL of 1.0 M in hexane) was added via syringe to 1.67 mL (11 mmol) of TMEDA in 20 mL of dry hexane in a dropping funnel. After 10 min, the BuLi/TMEDA solution was added to the [3]Fc dropwise at room temperature and then stirred overnight. At this point (next day), the mixture was a cloudy orange-red. The reaction mixture was cooled in dry ice/acetone and 1.3 mL (11.1 mmol) of distilled CF_2BrCF_2Br in 10 mL of dry hexane was added dropwise. The mixture was stirred at low temperature for 3 h and then warmed to room temperature at which time 2 mL of H_2O was added followed by 35 mL of CH_2Cl_2. The mixture was filtered and dried over Na_2SO_4 and the solvent removed. The material was filtered through a short silica column (3 in. × $^3/_4$ in.), and removal of solvent resulted in 1.2 g of crude product. The product mixture was chromatographed on a silica MPLC column by using 2.5% EtOAc/hexane as eluent. The first eluted was a mixture of starting material, 2-bromo[3]ferrocenophane (**14**), and 3-bromo[3]ferrocenophane (**13**). The second eluted was the 2,2′-dibromo[3]ferrocenophane (**16**) (310 mg, 18%) followed by the 3,3′-dibromo[3]ferrocenophane (**15**) (330 mg, 20%). The unseparated mixture was subsequently separated by HPLC on reverse-phase C-18 with 70% CH_3CN/H_2O. [3]Ferrocenophane (180 mg, 18%) was recovered first, followed by **13** (60 mg, 5%) and **14** (35 mg, 3%). **14** was recrystallized from cold pentane: mp 151–153 °C (lit.[30] mp 158–158.5 °C); ^1H NMR (400 MHz, $CDCl_3$) δ 4.38 (2 H, s), 4.09 (1 H, s), 4.06 (1 H, s), 3.99 (2 H, s), 3.58 (1 H, s), 2.29–2.33 (1 H, m), 1.91–2.11 (5 H, m); ^{13}C NMR ($CDCl_3$, trimethylene bridge) δ 22.4, 24.0, 34.8; IR (KBr) 2919, 2823, 1432, 874, 802, 508 cm^{-1}; mass spectrum, *m*/*z* (relative intensity) 306 (92), 304 (100), 225 (24.2); exact mass calcd $C_{13}H_{13}{}^{79}BrFe$ *m*/*z* 303.9550, found *m*/*z* 303.9553. **13** was recrystallized from cold pentane: mp 68.5–69.0 °C (lit.[30] mp 67–68 °C); ^1H NMR (400 MHz, $CDCl_3$) δ 4.32–4.40 (3 H, m), 4.31 (1 H, s), 3.99 (1 H, s), 3.93 (1 H, s), 3.82 (1 H, s), 1.80–2.05 (6 H, m); ^{13}C NMR ($CDCl_3$, trimethylene bridge) δ 24.1, 35.1; IR (KBr) 3082, 2930, 2900, 2845, 1440, 1037, 882, 822, 517 cm^{-1}; mass spectrum, *m*/*z* (relative intensity) 304 (100), 306 (92). Anal. Calcd for $C_{13}H_{13}BrFe$: C, 51.15; H, 4.26; Br, 26.23. Found: C, 49.71; H, 4.18; Br, 25.97. Difficulty was experienced in obtaining good analytical data for several of the halogenated ferrocenes (**11**, **12**, **13**) often owing to their instability. However, good analytical data was obtained for each of the target molecules (**2**–**6**) that were derived from the halogenated ferrocenes. **16** was recrystallized from benzene/hexane: mp 236 °C dec (lit.[30] mp 242 °C dec); ^1H NMR (400 MHz, $CDCl_3$) δ 4.35 (2 H, d, *J* = 1.5 Hz), 4.10 (2 H, t, *J* = 2.5 Hz), 3.99 (2 H, s), 2.34–2.41 (1 H, m), 1.82–2.04 (5 H, m); ^{13}C NMR ($CDCl_3$, trimethylene bridge) δ 21.8, 34.4; IR (KBr) 2910, 2850, 1434, 865, 794, 503 cm^{-1}; mass spectrum, *m*/*z* (relative intensity) 382 (56), 384 (100), 386 (50). Anal. Calcd for $C_{13}H_{12}Br_2Fe$: C, 40.63; H, 3.66. Found: C, 40.10; H, 3.10. **15** was recrystallized from benzene/hexane: mp 177–179 °C (lit.[30] mp 184.5–186 °C); ^1H NMR (400 MHz, $CDCl_3$) δ 4.40 (2 H, s), 4.35 (2 H, s), 4.00 (2 H, s), 1.82–2.03 (6 H, m); ^{13}C NMR ($CDCl_3$, trimethylene bridge) 23.9, 35.1; IR (KBr) 3090, 2915, 2840, 1434, 1383, 890, 802, 500 cm^{-1}; mass spectrum, *m*/*z* (relative intensity) 382 (56), 384 (100), 386 (47). Anal. Calcd for $C_{13}H_{12}Br_2Fe$: C, 40.63; H, 3.66. Found: C, 40.90; H, 3.24. Changing the stoichiometries to 1:1 [3]Fc:BuLi/TMEDA did not change the product ratios (determined by HPLC) but appreciably lowered the yields.

Mercuration of [3]Ferrocenophane. [3]Ferrocenophane (2 g, 8.85 mmol) was placed in a 500-mL, three-neck flask fitted with condenser, dropping funnel, and stir bar along with 45 mL of absolute methanol and 30 mL of dry ether. The mixture was heated, and mercuric acetate (1.14 g, 4.4 mmol) in 25 mL of hot MeOH was added dropwise over 1 h. The mixture was stirred for 6 h at reflux when heating was discontinued. LiCl (197 mg, 4.7 mmol) in 25 mL of hot MeOH was added over 10 min. Yellow precipitate formed immediately out of an orange solution. The contents were poured into a beaker, and solvent was removed under a stream of argon with gentle heating (overnight).

The resulting residue was extracted with hot hexanes (5 × 75 mL) to remove starting [3]ferrocenophane until the extracts were pale yellow. [3]Ferrocenophane (1.4 g, 70%) was recovered. The residue was then washed with hot H_2O followed by cold methanol and dried under argon. The resulting yellow powder (1.6 g) was put into a Soxhlet extractor and extracted with CH_2Cl_2. After 20 h, removal of solvent yielded 1.15 g of yellow-brown material. TLC (hexane/EtOAc, 2:1) revealed three components (with streaking and decomposition). Attempts to separate the components with CCl_4 and *n*-butyl alcohol were unsuccessful. The mixture was used in further preparations.

Bromination of Mercurated [3]Ferrocenophane. Mercurated [3]Fc (0.85 g—the mixture had at least two components, some of which may be dimercurated) was dissolved in 30 mL of DMF in a 250-mL, three-neck flask fitted with a dropping funnel. This was cooled in an ice bath and NBS (0.45 g, 2.5 mmol) in 30 mL DMF was added dropwise over 30 min. (Note: makeup of mercurated material is unclear, so an appreciable excess of NBS was used.) This was stirred for 2.5 h at 0 °C. Sodium thiosulfate in 10% aqueous solution (100 mL) was added to the reaction mixture. The brown solution turned yellow and was poured into 1 L of cold water. The aqueous solution was extracted with petroleum ether (10 × 100 mL). The petroleum ether extract was reduced to low bulk and chromatographed by using the "short-path" technique (2% EtOAc/hexane on 20 g of silica). Repeated chromatographs of the mixed fractions yield (based on unrecovered [3]Fc used to make starting [3]Fc–HgCl) 200 mg (50.2%) of 3-bromo[3]ferrocenophane (**13**) that was recrystallized from pentane: mp 68–69 °C (see section above entitled "Lithiation of [3]Ferrocenophane..." for complete analysis). Second eluted was 40 mg (11.6%) of 2-bromo[3]ferrocenophane (**14**). Also eluted was a trace of dibromo derivatives.

3-Iodo[3]ferrocenophane (11). *N*-Iodosuccinimide (NIS) (2.04 g, 9.1 mmol) in 200 mL of CH_2Cl_2 was added dropwise at 0 °C to 3.8 g (8.2 mmol assuming [3]Fc–HgCl) of mercurated [3]ferrocenophane (described previously). The reaction was allowed to warm to room temperature and was stirred overnight. To this was added 75 mL of 10% sodium bisulfite followed by 75 mL of 10% sodium carbonate. The layers were separated, and the aqueous portion was extracted with 3 × 50 mL portions of CH_2Cl_2. The combined organic layer was washed twice with 100 mL of 10% sodium carbonate and twice with 100 mL of H_2O and dried over $MgSO_4$. Solvent was removed, and the material was passed through a short silica column (5% THF/hexane) to yield 2.1 g of a yellow oil. TLC and HPLC showed three major components. Repeated chromatography using short-path techniques yield (based on starting [3]Fc–HgCl) 280 mg (15%) of recovered [3]ferrocenophane and 1.3 g (45%) of **11**: mp 53.5–55.0 °C (lit.[30] mp 52–53 °C); ^1H NMR (400 MHz, $CDCl_3$) δ 4.26–4.34 (4 H, m), 3.97 (2 H, br s), 3.64 (1 H, br s), 1.84–2.04 (6 H, m); IR (KBr) 3080, 2920, 2892, 2835, 1065, 870, 820, 530 cm^{-1}; mass spectrum, *m*/*z* (relative intensity) 353 (16.6), 352 (100), 225 (20.0); exact mass calcd for $C_{13}H_{13}FeI$ *m*/*z* 351.9413, found *m*/*z* 351.9405. Anal. Calcd for $C_{13}H_{13}FeI$: C, 44.32; H, 3.80. Found: C, 42.97; H, 3.69. Also eluted was 300 mg of a mixture, probably 2-I-[3]Fc and diiodo derivatives.

Mercuration of [4]Ferrocenophane. The same procedure detailed above for the mercuration of [3]ferrocenophane was used.

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(33) Turbitt, T. D.; Watts, W. E. *J. Organomet. Chem.* **1972**, *46*, 109–117.

(34) Roseblum, M.; Banerjee, A. K.; Danieli, N.; Fish, R. W.; Schlatter, V. *J. Am. Chem. Soc.* **1963**, *85*, 316–324.

When starting with 4.4 g (18.3 mmol) of [4]Fc, hexane extraction recovered 3.5 g (80%) of starting material. Extraction with methylene chloride yielded 1.2 g of brown solid. Again, the extract is a mixture that could not be separated by column chromatography or differences in solubility. This mixture was used in further preparations.

3-Iodo[4]ferrocenophane (12). The same procedure described for the synthesis of 3-I-[3]Fc was used here. NIS (496 mg, 2.2 mmol) in methylene chloride was added dropwise at 0 °C to 950 mg (2.0 mmol assuming composition is 100% [4]Fc–HgCl) of mercurated [4]ferrocenophane (from above). The mixture was allowed to warm to room temperature and stirred overnight. Workup yielded 430 mg of yellow oil. Repeated chromatography using short-path techniques with 2% THF/hexane as eluent allowed isolation of four fractions. The first was 40 mg (8%) of [4]ferrocenophane. The second was 230 mg (31%) of **12** as an orange oil: ^{1}H NMR 400 MHz ($CDCl_3$) δ 4.36 (1 H, br s), 4.30 (2 H, br s), 4.26 (1 H, br s), 4.10 (1 H, br s), 4.06 (1 H, br s), 3.69 (1 H, br s), 2.43 (4 H, m), 1.82 (4 H, m); mass spectrum, *m/z* (relative intensity) 367 (18.1), 366 (100), 239 (21.4), 183 (11.3), 119 (11.1); exact mass calcd for $C_{14}H_{15}FeI$ *m/z* 365.9570, found *m/z* 365.9569. Anal. Calcd for $C_{14}H_{15}FeI$: C, 45.90; H, 4.10. Found: C, 42.76; H, 3.88. The last two fractions were both mixtures (as evidenced by HPLC) and were unable to be purified. The third fraction (100 mg) contains 2-I-[4]Fc as determined from MS and by analogy to the [3]ferrocenophane case. The fourth fraction (40 mg) probably consists of diiodo derivatives.

[3].[3]Biferrocenophane (3) via Ullman Coupling. A mixture of 200 mg (0.57 mmol) of 3-iodo[3]ferrocenophane and 400 mg (6.3 mmol) of activated copper bronze[35] was placed in a Schlenk tube fitted with air condensor and was heated under argon to 140 °C for 16 h. The mixture was extracted with hot toluene until the washings were clear (about 200-mL total). The extract was filtered and removal of solvent gave 128 mg (quantitative) of **3** that was recrystallized from hexanes: mp 174.5–180 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 4.40–4.18 (8 H, m), 4.00 (2 H, d), 3.83 (2 H, br s), 3.69 (2 H, d), 1.70–2.02 (12 H, m); ^{13}C NMR ($CDCl_3$, trimethylene bridge) δ 24.4, 24.7, 35.2; IR (KBr) 3065, 2918, 2892, 2840, 1430, 1044, 808, 514 cm^{-1}; mass spectrum, *m/z* (relative intensity) 451 (33), 450 (100), 225 (12). Anal. Calcd for $C_{26}H_{26}Fe_2$: C, 69.33; H, 5.78. Found: C, 69.14; H, 5.93.

[4].[4]Biferrocenophane (6) via Ullman Coupling. The same procedure was used with 230 mg (0.63 mmol) of 3-iodo[4]ferrocenophane and 442 mg (6.9 mmol) activated copper bronze. Toluene extraction yielded 140 mg (93%) of **6** that was recrystallized from hexanes: mp 187–195 °C, ^{1}H NMR (400 MHz, $CDCl_3$) δ 4.30 (2 H, br s), 4.24 (2 H, br s), 4.16 (2 H, br s), 4.10 (4 H, m), 3.95 (2 H, br s), 3.52 (2 H, br s), 2.41 (4 H, br s), 2.35 (4 H, br s), 1.80 (8 H, br s); IR (KBr) 3065, 2918, 2832, 1440, 1030, 819, 500 cm^{-1}; mass spectrum, *m/z* (relative intensity) 479 (35), 478 (100), 372 (10), 358 (6), 239 (12). Anal. Calcd for $C_{28}H_{30}Fe_2$: C, 70.29; H, 6.28. Found: C, 70.57; H, 6.40.

[3].[0]Biferrocenophane (2). Ferrocenylzinc chloride was prepared by the following procedure of Rosenblum.[36] *n*-BuLi (2.8 mL of 2.2 M in hexane) was added to 1.5 g (5.7 mmol) of bromoferrocene in 20 mL of dry hexanes at room temperature and was stirred for 3 h when a precipitate formed. Hexanes was removed via syringe, and the precipitate was rinsed with 2 × 10 mL of dry hexanes. The ferrocenyllithium was then dissolved in 30 mL of dry THF resulting in a cherry-red solution. Zinc chloride, dissolved in 20 mL of dry THF, was added via syringe. This was stirred for 2–4 h. In a separate 250-mL, three-neck flask with gas inlet, condenser, septum, and stir bar was placed 1.0 g (2.8 mmol) of 3-iodo[3]ferrocenophane and 20 mg (0.028 mmol) of Pd(dppf)Cl_2 in 50 mL of dry THF. The ferrocenylzinc chloride solution was added via syringe and the mixture turned dark. This was stirred at gentle reflux for 48 h. Heating was discontinued, and 100 mL of 10% HCl was added. The mixture was extracted with ether; the ether extracts were washed with water and dried over $MgSO_4$. Removal of solvent resulted in 1.7 g of crude mixture. Chromatography using short-path techniques and 20% CH_2Cl_2/hexane as eluent yields 460 mg of ferrocene, 200 mg of 3-iodo[3]ferrocenophane, 60 mg of biferrocene, and 460 mg (50% based on unrecovered 3-I-[3]Fc) of **2**. Recrystallization gives 410 mg of a microcrystalline orange solid: mp 178–179 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 4.32 (2 H, br s), 4.26 (2 H, br s), 4.18 (2 H, br s), 4.13 (2 H, br s), 4.05 (5 H, s), 4.03 (1 H, br s), 3.85 (1 H, br s), 3.56 (1 H, br s), 1.82–2.06 (6 H, m); ^{13}C NMR ($CDCl_3$) (trimethylene bridge) δ 24.4, 24.7, 35.1; IR (KBr) 3065, 2922, 2878, 2840, 1438, 1106, 820, 498 cm^{-1}; mass spectrum, *m/z* (relative intensity) 408 (13), 410 (100), 411 (30). Anal. Calcd for $C_{23}H_{22}Fe_2$: C, 67.32; H, 5.37. Found: C, 67.14; H, 5.51.

[4].[0]Biferrocenophane (4). The same procedure was used as described above for the preparation of **2**. Ferrocenylzinc chloride was prepared from 506 mg (1.91 mmol) of bromoferrocene, 1.0 mL of 2.2 M *n*-BuLi in hexane, and 286 mg (2.1 mmol) of zinc chloride. This was added to a solution of 350 mg (0.96 mmol) of 3-iodo[4]ferrocenophane and 89 mg (0.01 mmol) of Pd(dppf)Cl_2 in 30 mL of dry THF. The reaction mixture was stirred at gentle reflux for 2 days. Workup was the same as described above. Short-path chromatography using 25% CH_2Cl_2/hexanes as eluent yields 110 mg of ferrocene, 30 mg (9%) of [4]ferrocenophane, 100 mg (29%) 3-iodo[4]ferrocenophane, and 140 mg (48%) of **4**. **4** was recrystallized from hexanes to give an orange solid: mp 163–164 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 4.35 (1 H, br s), 4.30 (2 H, br s), 4.17 (1 H, br s), 4.14 (2 H, br s), 4.10 (1 H, br s), 4.05 (1 H, br s), 4.01 (5 H, s), 3.99 (1 H, s), 3.96 (1 H, br s), 3.46 (1 H, br s), 2.35–2.46 (4 H, m), 1.81 (4 H, m); IR (KBr) 3065, 2920, 2840, 1492, 1109, 1040, 1003, 850, 822, 805, 492 cm^{-1}; mass spectrum, *m/z* (relative intensity) 425 (31), 424 (100), 422 (15). Anal. Calcd for $C_{24}H_{24}Fe_2$: C, 67.92; H, 5.66. Found: C, 67.96; H, 5.86.

[4].[3]Biferrocenophane (5). To a solution of 33 mg of 3-Br-[3]Fc (1.1 mmol) in 10 mL of THF at −78 °C was added 1.2 mL of *t*-BuLi (1.8 M in pentane). The mixture was stirred for 3 h at low temperature and then warmed to room temperature when 149 mg of zinc chloride (1.1 mmol) was added. Stirring was continued for three more hours. This solution was added via syringe to a mixture of 200 mg of 3-I-[4]Fc (0.55 mmol) and 8 mg (1.1×10^{-2} mmol) of $PdCl_2$(dppf) in 20 mL of dry THF. The reaction was warmed to a gentle reflux and stirred for 48 h. Workup was the same as described above for compound **2**. Short-path chromatography using 20% CH_2Cl_2/hexanes yields 90 mg of [3]Fc, 85 mg (44%) of 3-I-[4]Fc, 83 mg (32%) of **5**, and a trace of [3]Fc-[3]Fc (identified by HPLC). In addition, there was some strongly retained material that was not characterized. **5** was recrystallized from hexanes to give an orange solid: mp 170–185 °C; ^{1}H NMR (80 MHz, $CDCl_3$) δ 4.23 (8 H, m), 4.00 (2 H, m), 3.85 (2 H, m), 3.62 (2 H, m), 2.35 (4 H, m), 1.84 (10 H, m); IR (KBr) 3065, 2918, 2839, 1432, 1042, 811, 503 cm^{-1}; mass spectrum, *m/z* (relative intensity) 465 (34), 464 (100), 463 (6), 462 (15). Anal. Calcd for $C_{27}H_{28}Fe_2$: C, 69.82; H, 6.03. Found: C, 69.95; H, 6.22.

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Registry No. **1**, 1287-38-3; **2**, 107453-04-3; **3**, 107453-03-2; **4**, 107453-05-4; **5**, 107453-06-5; **6**, 107453-07-6; **7**, 12302-04-4; **9**, 33039-65-5; **11**, 82544-16-9; **12**, 107453-02-1; **13**, 82544-15-8; **14**, 82522-08-5; **15**, 82544-18-1; **16**, 82522-11-0; CF_2BrCF_2Br, 124-73-2; 2-ψ-[4]Fc, 107453-02-1; FcZnCl, 94161-76-9; Fc, 102-54-5; (Fc-Fc)$^+$, 51263-10-6; ([3]Fc-Fc)$^+$, 107453-08-7; ([4]Fc-Fc)$^+$, 107473-01-8; ([3]Fe-[4]Fc)$^+$, 107453-09-8; ([3]Fc-[3]Fc)$^+$, 107453-10-1; ([4]-Fc-[4]Fc)$^+$, 107453-11-2.

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