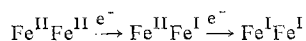


Reaction of Ferrocene with Polyaromatic Molecules. **π -Arenebis(π -cyclopentadienyliron) Dications. II. Electronic Structure**WILLIAM H. MORRISON, Jr., ELLEN Y. HO, and DAVID N. HENDRICKSON*¹

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Polarographic, electronic absorption and ⁵⁷Fe Mössbauer spectroscopic results are presented for a series of π -arene-bis(π -cyclopentadienyliron) dications. The electronic spectra of these compounds are found to be similar to the spectra of the corresponding π -arene- π -cyclopentadienyliron cations and to have d-d transitions analogous to ferrocene. The ⁵⁷Fe Mössbauer results for the π -arene-bis(π -cyclopentadienyliron) dications are also found to be similar to those for the π -arene- π -cyclopentadienyliron cations. In contrast, polarography indicates differences between the two in that many of the dications exhibit two iron reduction waves in addition to reduction waves for the arene; no oxidation waves were seen for these Fe(II) molecules up to the discharge of the electrolyte (+2.20 V vs. sce). The two reduction waves for the dications have been assigned as formally represented by the processes



The separation between these two half-waves is qualitatively discussed in terms of factors such as direct iron-iron electron-exchange interactions, ring-propagated exchange interactions, and direct dipolar iron-iron interactions. Three cases [*e.g.*, Fe₂(π -bibenzyl)(cp)₂²⁺] are noted where both iron centers reduce at the same potential. Asymmetric substitution on the polyaromatic molecule leads to large separations between the two iron reduction waves; for example, [(cp)-FePh](mesitylene)Fe(cp)₂²⁺ shows two one-electron waves at -1.13 and -1.50 V vs. sce.

Introduction

In the previous paper² in this series a general synthetic scheme for π bonding two (η^5 -C₅H₅)Fe moieties to certain polyaromatic molecules was introduced. Carbon-13 and proton nmr data were used to establish the molecular structure of the various dications. In this paper the electronic structure of these same π -arenebis(π -cyclopentadienyliron) dications will be characterized with polarographic measurements, electronic absorption, and ⁵⁷Fe Mössbauer spectroscopic data. This will be prefaced by an analysis of the electronic structure of the parent η^6 -benzenoid- η^5 -cyclopentadienyliron(II) cations. Attention will be directed to comparing the electronic structure of these Fe(II) species with that for ferrocene and bis(hexamethylbenzene)iron(II) dication. The comparison will be guided by ligand field theory (LFT), albeit a qualitative theory, but one quite adequate for the purpose at hand. This is the case, because we are mainly presenting experimental data most directly reflecting the molecular orbitals that are dominantly metal d orbital in construction. It is relevant to mention that LFT has been successfully applied³ to ferrocene and other low-spin d⁶ metallocenes; apparently, LFT has not been used on the bis(benzene)iron(II) dications. Also of importance is the large number of molecular orbital calculations for ferrocene⁴ and various bis(arene) complexes.⁵⁻⁸ Most recently, self-consistent extended Hückel calculations have been reported for metallocenes^{9,10} and bis(arenes).^{11,12} These calculations predict nuclear hyperfine coupling constants in reasonable agreement with experimental work and indicate that the highest filled molecular orbitals are predominantly metal d orbitals.

The major concern in this paper is, however, the electronic structure of the π -arenebis(π -cyclopentadienyliron) dications and whether these diiron species have any properties different from those of the π -arene-(π -cyclopentadienyliron) analogs. For example, formally mixed-valence [Fe^{II}Fe^{III}] biferrocene,¹³⁻¹⁵ biferrocenylenes,^{15,16} and [1.1]ferrocenophane¹⁷ compounds have been reported to have many interesting properties, properties not associated with either ferrocene or ferricenium ion. Polarographic data will be presented in this paper to demonstrate the potential of the various π -arene-bis(π -cyclopentadienyliron) dications to be reduced to formally [Fe^{II}Fe^I] mixed-valence compounds. The study of such d⁶-d⁷ mixed-valence species is important because it has not been

established whether the d⁵-d⁶ biferrocene-like systems are electron exchanging *via* direct Fe-Fe interactions or super-exchange interactions propagated by the fused cyclopentadienide rings. Thus, the d⁶-d⁷ system potentially has its unpaired electron largely localized on the d⁷ center in an e_{1g} molecular orbital which, although dominantly metal (d_{xz}, d_{yz}) in construction, has an appreciable ring contribution. On the other hand the d⁵-d⁶ system's unpaired electron would be on the d⁵ center in an e_{2g} molecular orbital which is essentially a nonbonding metal d orbital (d_{x²-y²}, d_{xy}).

Results and Discussion

Electronic Spectroscopy. A series of π -arenebis(π -cyclopentadienyliron) dications and various π -benzenoid- π -cyclopentadienyliron monocations were prepared (all are PF₆⁻ salts) and characterized as indicated in the previous paper.² Analytical data are given in Table I for those compounds which were not discussed in the previous paper. Ultraviolet-visible electronic absorption spectra were obtained for acetonitrile solutions of many of the compounds; the data are summarized in Table II.

Two types of electronic transitions have been identified in the uv-visible absorption spectrum of ferrocene.³ There are d-d transitions (three spin-allowed and one spin-forbidden) and ligand-to-metal charge-transfer transitions. In Figure 1 we have reproduced the spectra of the three low-spin d⁶ species Fe(cp)₂, Fe(cp)(benzene)⁺, and Fe(HMBZ)₂²⁺ (HMBZ = hexamethylbenzene). In each case there are in the visible region low-intensity bands assignable to spin-allowed d-d transitions. Three spin-allowed transitions (¹A_{1g} → ¹A¹E_{1g}, ¹E_{2g}, ¹E_{1g}) are expected for ferrocene. Ferrocene shows two band systems at 22,700 and 30,800 cm⁻¹; the lower energy band has been shown³ by low-temperature measurements to be composed of two spin-allowed d-d transitions (21,800 and 24,000 cm⁻¹).

In the spectra of Fe(cp)(benzene)⁺ and Fe(HMBZ)₂²⁺ it is also possible to identify for each species three peaks in the visible region assignable to spin-allowed d-d transitions. The symmetries of Fe(cp)(benzene)⁺ and Fe(HMBZ)₂²⁺ are obviously different from that (*D*_{5d}) determined for Fe(cp)₂. If Fe(HMBZ)₂²⁺ has *D*_{6d} symmetry (staggered), three spin-allowed d-d transitions (¹A₁ → ¹A¹E₅, ¹E₃, and ¹E¹E₅) are expected in direct analogy with the Fe(cp)₂ case. However, if Fe(HMBZ)₂²⁺ can be considered to have *D*_{6h} symmetry (eclipsed), then one of the degenerate excited states would

Table I. Analytical Data for PF_6^- Salts of $\text{Fe}(\text{cp})$ -Substituted Aromatic Compounds and for Related Compounds

Substituted arene	Compd	% calcd			% found		
		C	H	Fe	C	H	Fe
Chlorobenzene	$\text{C}_{11}\text{H}_{10}\text{ClFe}(\text{PF}_6)^a$	34.91	2.66	14.76	35.40	2.74	14.78
<i>trans</i> -Stilbene	$\text{C}_{24}\text{H}_{22}\text{Fe}_2(\text{PF}_6)_2$	40.48	3.11	15.69	40.72	3.33	15.58
1,1'-Binaphthyl	$\text{C}_{30}\text{H}_{24}\text{Fe}_2(\text{PF}_6)_2$	45.84	3.08	14.21	45.84	3.11	14.02
Phenylmesitylene	$\text{C}_{25}\text{H}_{26}\text{Fe}_2(\text{PF}_6)_2$	41.24	3.60	15.34	41.63	3.81	14.09
	$[\text{Fe}(\text{HMBZ})_2](\text{PF}_6)_2$	43.00	5.41	8.33	42.80	5.58	8.30
	$[\text{Fe}(\text{HMBZ}(\text{cp}))](\text{PF}_6)$	47.69	5.41	13.04	48.00	5.59	12.35
	$[\text{Fe}_2(\text{benzene})_2(\text{fulvalene})](\text{PF}_6)_2$	38.52	2.94	16.28	39.59	2.80	15.51

^a Chlorine analysis: calcd, 9.37; found, 9.14.

Table II. Electronic Absorption Data for π -Arene- π -cyclopentadienyliron (1+) and π -Arenebis(π -cyclopentadienyliron) (2+) Compounds^a

Compd	Band, cm^{-1}	ϵ , l. mol ⁻¹ cm ⁻¹	Assignment	Compd	Band, cm^{-1}	ϵ , l. mol ⁻¹ cm ⁻¹	Assignment
$\text{Fe}(\text{HMBZ})_2^{2+}$	18,700 sh	38	d-d	$\text{Fe}_2(\text{fluorene})(\text{cp})_2^{2+}$	21,500 sh	346	d-d
	21,900	96	d-d		25,300	958	d-d
	30,800	3,360	d-d		30,800 sh	5,150	d-d
	39,300	6,750			33,600 sh	9,460	
	42,400	46,700			34,800 sh	10,800	
	>50,000				39,100	28,500	
$\text{Fe}(\text{HMBZ})(\text{cp})^+$	22,000 sh	64.4	d-d	$\text{Fe}_2(\text{trans-stilbene})(\text{cp})_2^{2+}$	40,000 sh	26,700	
	24,700	80.7	d-d		42,300	20,900	
	31,200 sh	144	d-d		>50,000		
	37,900 sh	2,280			21,500 sh	269	d-d
	41,100	11,000			25,500	856	d-d
	>50,000				29,100 sh	2,540	d-d
$\text{Fe}(\text{benzene})(\text{cp})^+$	22,200	68.4	d-d	$\text{Fe}_2(1,1'\text{-binaphthyl})(\text{cp})_2^{2+}$	33,400 sh	5,630	
	26,200	86.2	d-d		38,200 sh	12,000	
	31,900 sh	230	d-d		41,400	26,800	
	38,200 sh	2,580			>50,000		
	41,800	11,700			20,600	677	d-d
	>50,000				23,100	626	d-d
$\text{Fe}(\text{chlorobenzene})(\text{cp})^+$	22,100	66	d-d	$\text{Fe}_2(\text{chrysene})(\text{cp})_2^{2+}$	28,500 sh	3,450	d-d
	25,900	92	d-d		30,600 sh		
	32,800 sh	1,000	d-d		34,200 sh		
	37,000 sh	2,320			35,700 sh		
	41,500	19,100			39,400	29,900	
	>50,000				45,600	94,600	
$\text{Fe}(\text{biphenyl})(\text{cp})^+$	22,600 sh	138	d-d	$\text{Fe}_2(\text{anthracene})(\text{cp})_2^{2+}$	>50,000		
	25,700 sh	277	d-d		20,400	786	d-d
	30,300 sh	1,200	d-d		23,600 sh		d-d
	35,500 sh	6,000			29,900 sh	8,060	d-d
	39,500	18,900			31,700 sh		
	42,800	16,600			33,300 sh		
$\text{Fe}(\text{naphthalene})(\text{cp})^+$	>50,000			34,400 sh			
	20,800	187	d-d	35,500	28,100		
	22,900 sh	171	d-d	37,500	77,800		
	28,600	902	d-d	38,800	55,500		
	32,500 sh	2,350		>50,000			
	35,100 sh	4,500		23,200 sh	182	d-d	
$\text{Fe}_2(\text{biphenyl})(\text{cp})_2^{2+}$	36,600 sh	6,810		27,400	564	d-d	
	40,100	11,200		31,800 sh		d-d	
	42,900	12,500		34,200 sh			
	>50,000			36,800 sh			
	22,000 sh	312	d-d	41,200	23,800		
	25,500	843	d-d	>50,000			
$\text{Fe}_2(\text{phenanthrene})(\text{cp})_2^{2+}$	30,800 sh	3,120	d-d	21,100 sh	426	d-d	
	40,500	29,300		24,000 sh	777	d-d	
	>50,000			29,000	5,390	Arene α or d-d	
				34,400 sh	9,660		
				39,600	27,300		
				44,900 sh	4,620		
			>50,000				

^a All compounds were run as PF_6^- salts dissolved in acetonitrile at room temperature.

theoretically be split giving four transitions ($^1A_{1g} \rightarrow a^1E_{1g}$, $^1B_{1g}$, $^1B_{2g}$, b^1E_{1g}). We have elected to assume that this splitting would be negligibly small and have therefore used the ferrocene transition energy expressions³ to analyze the d-d part of the spectrum of $\text{Fe}(\text{HMBZ})_2^{2+}$. The same assumption was made for the $\text{Fe}(\text{cp})(\text{benzene})^+$ ion. Scott and Matsen¹⁸ have shown that metallocenes, bis(arene)metal compounds, and other related complexes can be treated as if they possessed an effective axial ($C_{\infty v}$) symmetry.

Figure 1 shows that, contrary to the ferrocene case, the first band systems in the spectra of $\text{Fe}(\text{cp})(\text{benzene})^+$ and $\text{Fe}(\text{HMBZ})_2^{2+}$ are clearly resolved into two peaks even at room temperature. The near degeneracy of two bands in the ferrocene case is after all merely accidental. It should also be noted that the band assigned as the highest energy d-d transition in $\text{Fe}(\text{HMBZ})_2^{2+}$ at 30,800 cm^{-1} has an extinction of ϵ 3360 l. mol⁻¹ cm⁻¹. In spite of the magnitude of ϵ for this band, there does not seem to be any other reasonable as-

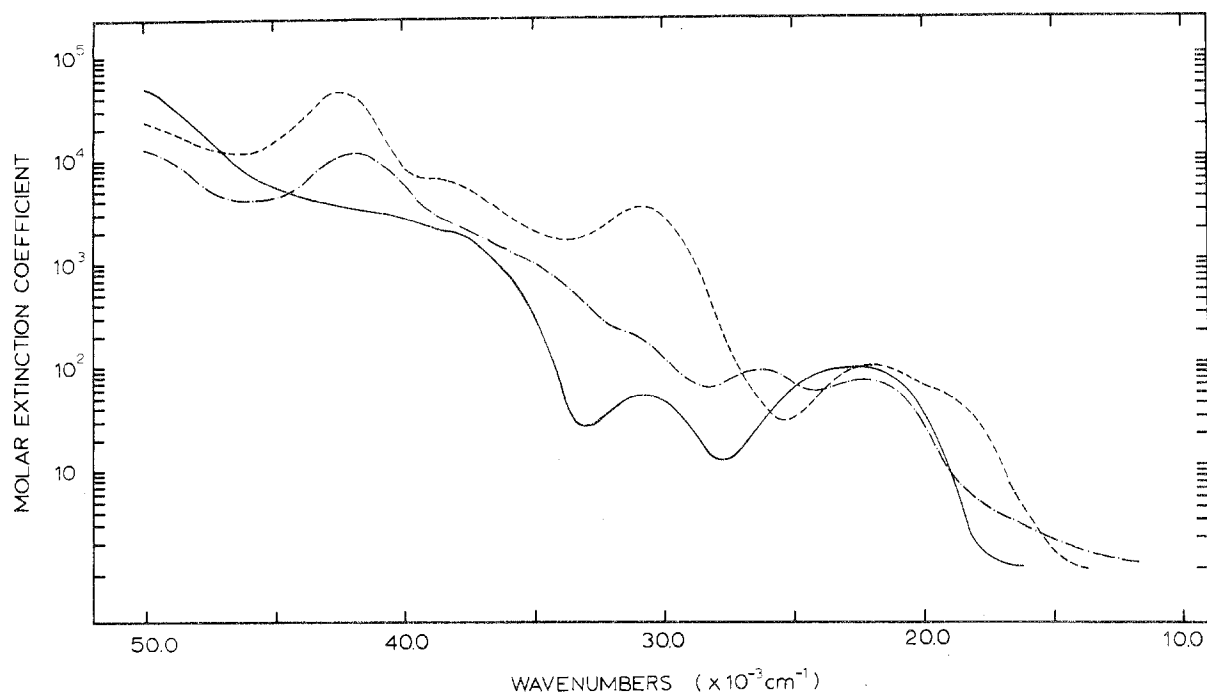
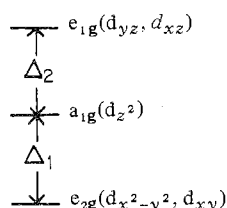


Figure 1. Electronic absorption spectra for three Fe(II) complexes in acetonitrile solution at 300°K: Fe(cp)₂, —; [Fe(cp)(benzene)](PF₆), ---; [Fe(HMBZ)₂](PF₆)₂, - · -.

signment for this band than a spin-allowed d-d transition. The large extinction is most likely due to greater mixing (intensity borrowing) of the ring orbitals and metal d orbitals expected for the benzenoid compounds. In addition, it is possible to identify, by comparison with the Fe(cp)₂ spectrum, bands at 42,400 and 41,100 cm⁻¹ clearly assignable to $\pi \rightarrow \pi^*$ benzene transitions for Fe(HMBZ)₂²⁺ and Fe(cp)(benzene)⁺, respectively. The proximity of this band to the highest energy d-d band in Fe(HMBZ)₂²⁺ substantiates the hypothesis that the large ϵ for the highest energy Fe(HMBZ)₂²⁺ d-d band is due to intensity borrowing.

The three visible transitions observed for both Fe-(HMBZ)₂²⁺ and Fe(cp)(benzene)⁺ were assigned analogously to Fe(cp)₂ where the transition energy increases in the series ($a^1E_{1g} \leftarrow ^1A_{1g}$) < ($^1E_{2g} \leftarrow ^1A_{1g}$) < ($b^1E_{1g} \leftarrow ^1A_{1g}$). The one-electron core energies of the d orbitals in these molecules can be expected to be ordered as follows



The two ligand field splitting parameters, $\Delta_1 = \epsilon^e(a_{1g}-e_{2g})$ and $\Delta_2 = \epsilon^e(e_{1g}-a_{1g})$, and the electron repulsion parameter B (we have assumed that $C/B = 4.0$) have been evaluated from the positions of the three d-d bands. The parameters resulting from such an analysis are reported in Table III for the molecules whose electronic spectra are summarized in Table II. The value of Δ_1 is appreciably larger for Fe(HMBZ)₂²⁺ than it is for ferrocene, which is in agreement with recent MO calculations¹² where the increase was attributed to an increased bonding interaction between the filled e_{2g} dominantly metal orbitals and the appropriate benzene ring orbitals. The mixed Fe(cp)(HMBZ)⁺ and Fe(cp)(benzene)⁺ ions have intermediate Δ_1 values. Apparently, the chlorine atom in Fe(cp)(chlorobenzene)⁺ withdraws electrons from the benzene ring to such an extent that the ring orbitals in this more positively charged benzene system interact more with the metal e_{2g} orbitals

Table III. Ligand Field Parameters (cm⁻¹) for Arene Complexes

Compd	Δ_1	Δ_2	B
Fe(cp) ₂	7100	22,000	390
Fe(HMBZ) ₂ ²⁺	9300	18,800	470
Fe(HMBZ)(cp) ⁺	7700	22,000	380
Fe(benzene)(cp) ⁺	8500	21,900	320
Fe(biphenyl)(cp) ⁺	7000	22,400	280
Fe(naphthalene)(cp) ⁺	6300	20,900	330
Fe(chlorobenzene)(cp) ⁺	9400	21,900	420
Fe ₂ (biphenyl)(cp) ₂ ²⁺	8000	21,700	330
Fe ₂ (anthracene)(cp) ₂ ²⁺	8300	22,800	280
Fe ₂ (trans-stilbene)(cp) ₂ ²⁺	7500	21,100	240

increasing Δ_1 for Fe(cp)(chlorobenzene)⁺ to 9400 cm⁻¹. The arene rings bonded to the iron in the single iron species Fe-(cp)(biphenyl)⁺ and Fe(cp)(naphthalene)⁺ would be expected to possess relatively more negative charge density than in Fe(cp)(benzene)⁺ and thus smaller Δ_1 values are found; the Δ_1 values for these two mixed cations are even smaller than or comparable to that for ferrocene. A cautionary note should be added. As can be seen in Table II, many of the d-d bands for Fe(cp)(biphenyl)⁺ and Fe(cp)(naphthalene)⁺ appear as shoulders of intense features in the near-uv spectra and as such the uncertainties in the band positions and resulting ligand field parameters are large (Δ_1 and Δ_2 are determined to approximately ± 200 cm⁻¹).

The values of the electron repulsion parameter B obtained for these arene-cyclopentadienyl molecules indicate appreciable covalency as found for ferrocene.³ It is interesting to note that the largest B is found for Fe(HMBZ)₂²⁺.

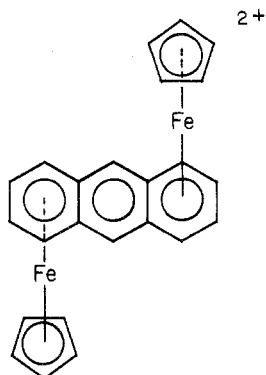
Of the "d levels" in ferrocene the antibonding e_{1g} level probably has the greatest ring character. The recent MO calculations¹² point to a decreased interaction between the e_{1g} metal orbitals and the appropriate symmetry ring orbitals for the bis(arene) complex in comparison to the bis(cyclopentadienide) complex. Thus, we find that Δ_2 is smaller for Fe(HMBZ)₂²⁺ than for Fe(cp)₂. The mixed arene-cyclopentadienyl complexes have Δ_2 values that are closer to that for ferrocene. In summary, it is clear from an analysis of the "d-d" transitions in the above molecules that the basic features of the ligand field interactions are quite similar. Even further, inspection of the visible electronic data in Tables II and III

Table IV. Mössbauer Parameters

Compd	Temp, °K	δ , ^{a,b} mm/sec	ΔE_Q , ^b mm/sec
Fe ₂ (biphenyl)(cp) ₂ ²⁺	300	0.441 (3)	1.555 (3)
	4.2	0.536 (1)	1.601 (1)
Fe ₂ (pyrene)(cp) ₂ ²⁺	300	0.477 (1)	1.667 (3)
	4.2	0.564 (1)	1.673 (1)
Fe(benzene)(cp) ⁺ ^c	77	0.57 (5)	1.67 (5)
Fe(biphenyl)(cp) ⁺ ^c	77	0.51 (5)	1.45 (5)
Fe(mesitylene) ₂ ²⁺ ^c	77	0.59 (5)	1.95 (5)
Fe(naphthalene)(cp) ⁺ ^c	77	0.62 (5)	1.76 (5)

^a The isomer shift is referenced to iron foil. ^b The numbers in parentheses are estimated relative errors from a Lorentzian fitting program. Absolute errors are ~0.2%. ^c From ref 19, these are BF₄⁻ salts, except the mesitylene compound which is a BPh₄⁻ salt.

for the π -arenebis(π -cyclopentadienyliron) dications shows that there is nothing unusual in the ligand field characteristics of these dications. More specifically, in the molecule



(whether both Fe(cp) moieties are on the same or opposite sides of the anthracene plane has *not* been established) the outer fused rings do afford the iron a ligand field similar to that found in the single-iron arene-cyclopentadienyl complexes.

In the uv electronic spectra of the molecules in Table II absorptions are seen that are due primarily to the arene. For example, Fe(cp)(benzene)⁺ shows two bands at 38,200 and 41,800 cm⁻¹ which could correspond to the two bands seen in free benzene at 39,400 and 49,100 cm⁻¹. The extinction coefficients of both of these Fe(cp)(benzene)⁺ transitions are considerably greater than those for free benzene, $\epsilon(39,400 \text{ cm}^{-1}) 204 M^{-1} \text{ cm}^{-1}$ and $\epsilon(49,100 \text{ cm}^{-1}) 7400 M^{-1} \text{ cm}^{-1}$. It can be seen from Figure 1 and Table II that ferrocene has some weak charge-transfer transitions in this same region, and if Fe(cp)(benzene)⁺ also has weak ring \rightarrow iron transitions in this region, this would account for the apparent enhanced intensities of the bands associated with the coordinated arene moiety. A comparison of the uv characteristics of Fe(cp)(biphenyl)⁺ and Fe₂(cp)₂(biphenyl)²⁺ is interesting. The latter ion has an intense uv transition at 40,500 cm⁻¹, associated with the two Fe(cp)-substituted rings of the biphenyl moiety. The monosubstituted biphenyl cation has a transition at 39,500 cm⁻¹ for the substituted benzene and peaks at 42,800 and 35,500 cm⁻¹ for the unsubstituted benzene of the biphenyl moiety. All of the molecules in Table II show "end absorption" at energies >50,000 cm⁻¹, in analogy to ferrocene³ where this feature has been assigned to a spin- and symmetry-allowed ligand-to-iron charge transfer, ¹A_{1u} \leftarrow ¹A_{1g}.

Iron-57 Mössbauer Spectra. Samples of the PF₆⁻ salts of Fe₂(cp)₂(biphenyl)²⁺ and Fe₂(cp)₂(pyrene)²⁺ were studied by ⁵⁷Fe Mössbauer spectroscopy. The spectrum of the biphenyl system is reproduced in Figure 2 and data from the least-squares fitting of the spectra of both samples are presented in Table IV along with representative literature data. There are two points of interest: the variation in quadrupole splitting (ΔE_Q) in ferrocene and the iron(II)-arene compounds and a

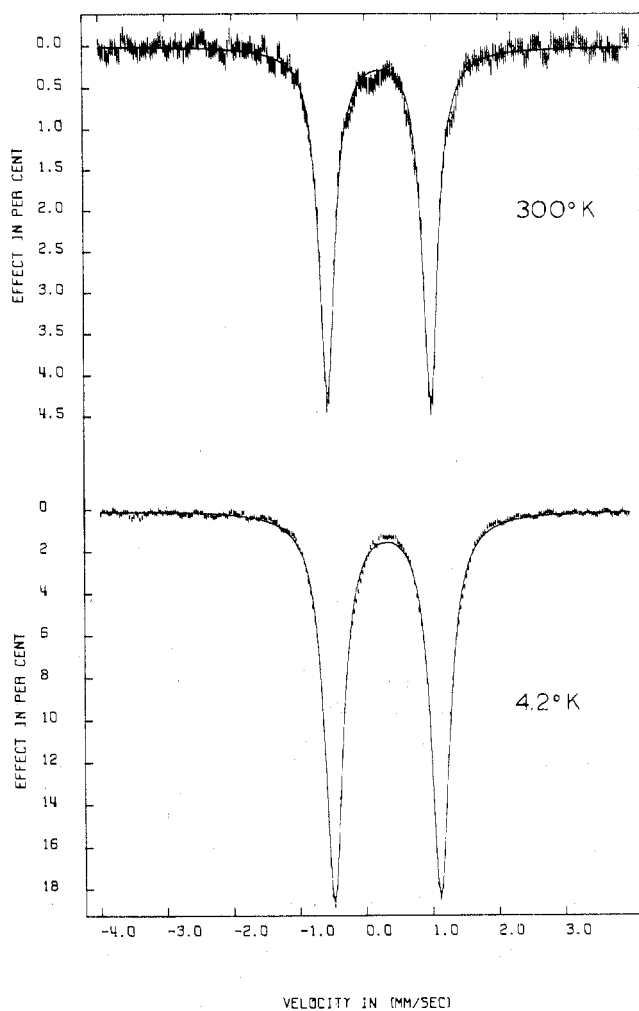


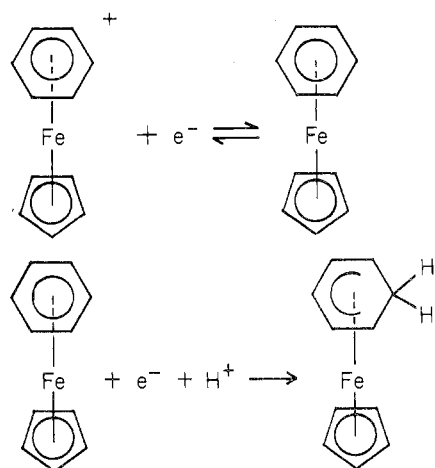
Figure 2. Iron-57 Mössbauer spectra at two different temperatures for [Fe₂(biphenyl)(cp)₂](PF₆)₂. Velocity scale is referenced to Co in Cu source.

comparison of the data for Fe(cp)(arene)⁺ and Fe₂(cp)₂(arene)²⁺.

Ferrocene has a quadrupole splitting of 2.4 mm/sec and a positive electric field gradient, both of which can be rationalized, in a valence-electron-only explanation, by noting that ferrocene has the "d-electron" configuration (a_{1g})²(e_{2g})⁴ and by assuming that $V_{zz}(a_{1g}) = -4/7\langle r^{-3} \rangle$ and $V_{zz}(e_{2g}) = 4/7\langle r^{-3} \rangle$. Gol'danskii, *et al.*,¹⁹ have reported Mössbauer data for various Fe(cp)(arene)⁺ compounds and for Fe(mesitylene)₂²⁺; see Table IV. The reduction in ΔE_Q in going from ferrocene to Fe(mesitylene)₂²⁺ was attributed to a greater interaction in the latter case of the e_{2g} d orbitals with the ring orbitals, in effect reducing the electron density in the e_{2g} d orbitals and thus the positive contribution to the field gradient V_{zz} . This analysis is in agreement with the recent MO calculations¹² as well as our evaluation of Δ_1 parameters in the last section. Inspection of Table IV shows that the mixed Fe(cp)(arene)⁺ systems have even smaller ΔE_Q values than Fe(mesitylene)₂²⁺, even though we found the Δ_1 values for Fe(cp)(arene)⁺ to be intermediate between those for Fe(cp)₂ and Fe(HMBZ)₂²⁺. Even further, the relatively low Δ_1 values for Fe(cp)(biphenyl)⁺ and Fe(cp)(naphthalene)⁺ are not reflected in their ΔE_Q values. All of these inconsistencies are probably related to the approximations involved in the above qualitative analysis of ΔE_Q . Such an analysis would work for cases where there is a large change in ΔE_Q (e.g., ferrocene to ferricenium), but for relatively small changes it is necessary to account for many other factors influencing ΔE_Q .

Most important to this work is the comparison of ΔE_Q and

Scheme I



δ values for $\text{Fe}(\text{cp})(\text{biphenyl})^+$ vs. $\text{Fe}_2(\text{cp})_2(\text{biphenyl})^{2+}$. There seems to be little change in Mössbauer parameters as the number of $\text{Fe}(\text{cp})^+$ moieties increases. In addition, the temperature dependencies of δ and ΔE_Q for the two iron species do not seem to be unusual. In summary, neither electronic absorption spectroscopy nor ^{57}Fe Mössbauer spectroscopy indicates any properties of the two-iron systems that reflect the presence of two metal centers.

Electrochemistry. Polarographic measurements, employing a dropping-mercury electrode (dme), were carried out on an extended series of $\text{Fe}_2(\text{cp})_2(\text{arene})^{2+}$ species (PF_6^- salts dissolved in acetonitrile with 0.1 M $(\text{C}_2\text{H}_5)_4\text{N}(\text{ClO}_4)$ as electrolyte) and in the following we will show that the $\text{Fe}_2(\text{cp})_2(\text{arene})^{2+}$ ions do show polarographic characteristics indicative of the influence of one iron on the second iron, that is, evidence for potentially $[\text{Fe}^{\text{II}}\text{Fe}^{\text{I}}]$ mixed-valence compounds.

Both dc and differential-pulse polarographies were used in this study. When feasible, the reversibility of the various half-waves was determined by the slope of potential vs. $\log [i/(i_d - i)]$ plots. The number of electrons involved was determined by comparing the diffusion current of the arene complexes with that for a ferrocene solution of equal concentration and from constant-potential electrolysis experiments. The results of these studies are summarized in Table V.

Nesmeyanov, *et al.*,²⁰ found that the $\text{Fe}(\text{cp})(\text{arene})^+$ ions are extremely stable toward oxidation and as such it was not too surprising that we have also found the $\text{Fe}_2(\text{cp})_2(\text{arene})^{2+}$ ions to be resistant to oxidation. No oxidation is seen for the $\text{Fe}_2(\text{cp})_2(\text{arene})^{2+}$ ions at a rotating platinum electrode up to the discharge of the electrolyte ($\sim +2.20$ V vs. sce). The $\text{Fe}(\text{cp})(\text{arene})^+$ ions are, however, known to exhibit two one-electron reduction waves at a dme.²¹ The first wave (reversible) has been attributed to the reduction of the iron from Fe(II) to Fe(I) to give an uncharged complex, and the second more negative wave (irreversible), to the reduction of the arene (see Scheme I). For $\text{Fe}(\text{cp})(\text{benzene})^+$, the first wave is found at -1.45 V and the second at -2.39 V, both vs. sce. The limiting current of the second wave was shown to be a function of the concentration of H^+ and the final product is diamagnetic cyclohexadienylcyclopentadienyliron(II). The overall process can be viewed as a hydride addition to the coordinated arene; Watts, *et al.*,²² have studied the stereospecificity of the hydride addition for various substituted arenes using proton nmr. Dark green air-sensitive $\text{Fe}(\text{cp})(\text{arene})$ compounds, formally containing Fe(I), have very recently been prepared.²³

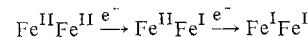
We have found that the $\text{Fe}_2(\text{cp})_2(\text{arene})^{2+}$ ions also show similar reductive electrochemistry. There are reversible waves, one or two depending on the particular compound, in the region of ~ -0.9 to ~ -1.5 V probably associated with reduction of

Table V. Electrochemical Data on π -Arenebis(π -cyclopentadienyliron) Systems^a

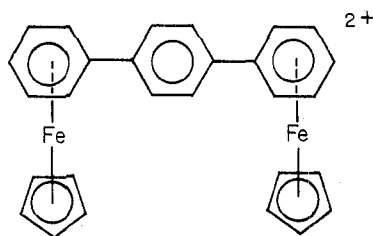
Compd	$E_{1/2}$, V		Slope, ^b mV
	Dc	Dp	
$\text{Fe}_2(\text{benzene})_2(\text{bicyclopentadienyl})^{2+}$ ^c		-1.18	1
$\text{Fe}_2(\text{biphenyl})(\text{cp})_2^{2+}$		-1.58	1
		-1.17	1
		-1.32	1
$\text{Fe}_2(1,1'\text{-binaphthyl})(\text{cp})_2^{2+}$		-2.13	1
		-0.96	1
		-1.07	1
$\text{Fe}_2(1,2:4,5\text{-dibenzo-1,4-cycloheptadiene})(\text{cp})_2^{2+}$		-1.68	1
		-1.39	1
		-1.50	1
$\text{Fe}_2(\text{biphenylmethane})(\text{cp})_2^{2+}$		-2.25	1
		-1.35	1
		-1.37	1
$\text{Fe}_2(\text{fluorene})(\text{cp})_2^{2+}$		-1.47	1
		-1.46	1
		-2.21	2
$\text{Fe}_2(9,10\text{-dihydroanthracene})(\text{cp})_2^{2+}$		-1.19	1
		-1.43	1
		-1.50	1
$\text{Fe}_2(\text{anthracene})(\text{cp})_2^{2+}$		-2.18	2
		-1.33	1
		-1.35	1
$\text{Fe}_2(\text{chrysene})(\text{cp})_2^{2+}$		-1.49	1
		-1.49	1
		-2.27	4
$\text{Fe}_2(\beta\text{-phenylnaphthylene})(\text{cp})_2^{2+}$		-1.34	1
		-1.34	1
		-1.48	1
$\text{Fe}_2(p\text{-terphenyl})(\text{cp})_2^{2+}$		-0.90	1
		-0.97	1
		-1.16	1
$\text{Fe}_2(\text{trans-stilbene})(\text{cp})_2^{2+}$		-1.42	1
		-1.69	1
		-1.13	1
$\text{Fe}_2(\text{biphenyl})(\text{cp})_2^{2+}$		-1.50	1
		-0.97	1
		-1.38	2
$\text{Fe}_2(\text{biphenyl})(\text{cp})_2^{2+}$		-2.02	1
		-1.36	2
		-2.20	2
$\text{Fe}_2(\text{biphenyl})(\text{cp})_2^{2+}$		-1.47	2
		-2.23	4
		-1.44	2
$\text{Fe}_2(3,3',4,4'\text{-tetramethylbiphenyl})(\text{cp})_2^{2+}$		-2.22	3
		-1.22	1
		-1.57	1

^a The half-wave potentials are vs. a saturated aqueous calomel electrode; dc stands for direct current while dp stands for differential pulse and n is the number of electrons. ^b This is the slope of the potential (E) vs. $\log [i/(i_d - i)]$ plot. ^c This complex is formed in the reaction between benzene and biferrocene where the fused bicyclopentadienyl ring is retained.

the iron atoms, and a more negative wave due to the reduction of the arene. As can be seen in Table V, many of the $\text{Fe}_2(\text{cp})_2(\text{arene})^{2+}$ species show two reduction waves due to the sequential reduction of the two iron centers



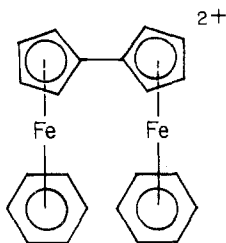
This is analogous to the oxidation characteristics of various bridged biferrocenes as we reported¹⁴ recently. The separation between the two biferrocene oxidation half-waves was viewed as being due to three effects: (1) direct iron-iron electron-exchange interactions, (2) iron-iron dipolar interactions, and (3) electron-exchange interactions propagated through the rings. A similar qualitative analysis can be advanced to explain the data in Table V. The $\text{Fe}_2(\text{cp})_2(\text{arene})^{2+}$ systems with large Fe-Fe distances and weak ring-propagated exchange interaction owing to little conjugation between the phenyl rings are seen to have only a single two-electron reversible wave for iron reduction. Thus, in the cases of $\text{Fe}_2(\text{cp})_2(\text{arene})^{2+}$ where arene = biphenyl, *trans*-stilbene, and *p*-terphenyl there is only one wave at -1.47 , -1.47 , and -1.36 V vs. sce, respectively. The structure of the last ion has been shown² by ^{13}C nmr to be



Both Fe(II) centers in these three molecules reduce at the same potential.

Two half-waves with a separation of ~ 0.15 V are seen for the $\text{Fe}_2(\text{cp})_2(\text{arene})^{2+}$ ions with fused aromatic rings, even though they probably have relatively large iron-iron distances. Examples of such ions can be found when the arene is either anthracene or chrysene. The two $\text{Fe}(\text{cp})^+$ moieties in these molecules are most likely on opposite sides of the arene plane² and as such there are large Fe-Fe distances. The electronic spectroscopy section has shown that there is appreciable metal-ring covalency in the $\text{Fe}_2(\text{cp})_2(\text{arene})^{2+}$ ions. Perhaps the separation in half-waves for these ions with large Fe-Fe distances is due to a stabilization of the $\text{Fe}^{\text{II}}\text{Fe}^{\text{I}}$ state (i.e., the d^6-d^7 state) of the system, a stabilization resulting from superexchange-type interactions propagated by the extended arene. Thus, there is a certain degree of "spin polarization" of the unpaired d^7 electron out onto the arene and then to the d^6 metal center and this stabilizes the system. It still remains to show that, in fact, the dication with the arene as anthracene or chrysene have the $\text{Fe}(\text{cp})^+$ moieties on opposite sides of the arene plane. Recent work in our laboratories has indicated that the electron-transfer rate in partially oxidized biferrrocene-like systems reflects the level of direct Fe-Fe exchange-type interaction. It is to be noted that the unpaired electron in a d^5-d^6 system is in a quite different orbital.

An appreciable half-wave separation is also found for the $\text{Fe}_2(\text{cp})_2(\text{arene})^{2+}$ ions when the Fe-Fe distance is small, even though the "resonance" ring interaction is small. The molecule $\text{Fe}_2(\text{cp})_2(\text{biphenyl})^{2+}$ has two waves with a separation of 0.10 V; there is probably little ring-propagated interaction because the C-C bond between the phenyl moieties in biphenyl, as determined by X-ray work, approximates to a single bond. Reaction of biferrrocene with excess benzene gives the $\text{Fe}_2(\text{benzene})_2(\text{bicyclopentadienyl})^{2+}$ cation (¹³C nmr spectrum in agreement with formulation)



This species exhibits two iron reduction waves with an even greater separation of 0.40 V, which could be a result of potentially closer iron-iron approach with perhaps some ring-propagated interaction. All in all, for many of the $\text{Fe}_2(\text{cp})_2(\text{arene})^{2+}$ ions the separation between the two iron reduction waves appears qualitatively to reflect the degree of arene-propagated superexchange and through-space effects from short Fe-Fe distances. Without X-ray structural work it is not possible, at present, quantitatively to check this rule. The $\text{Fe}_2(\text{cp})_2(9,10\text{-dihydroanthracene})^{2+}$ ion shows two waves with a separation of 0.14 V and in our previous paper we have shown with proton nmr that the $\text{Fe}(\text{cp})^+$ moieties are on opposite sides of the 9,10-dihydroanthracene molecular plane. There should not be much inter-ring conjugation in this molecule.

The largest iron reduction wave separations are obtained, as would be expected, for the asymmetrically substituted arenes (see Table V). Nesmeyanov, *et al.*,²¹ did find that the position of the first reduction wave for $\text{Fe}(\text{cp})(\text{arene})^+$ varied considerably with the nature of substituents on the arene or cyclopentadienide. Electron-withdrawing substituents shifted the potential to more positive values and *vice versa* for electron-donating groups. We find that $\text{Fe}_2(\text{cp})_2(\text{phenylmesitylene})^{2+}$ has two waves at -1.13 and -1.50 V vs. sce; similarly, there are two waves at -0.97 and -1.38 V for $\text{Fe}_2(\text{cp})_2(\beta\text{-phenylnaphthalene})^{2+}$. These large separations should facilitate isolation of potentially $[\text{Fe}^{\text{II}}\text{Fe}^{\text{I}}]$ mixed-valence compounds and work is in progress in this area.

A comparison of $E_{1/2}$ values for $\text{Fe}_2(\text{cp})_2(\text{arene})^{2+}$ and the corresponding $\text{Fe}(\text{cp})(\text{arene})^+$ values, when available, is interesting. Nesmeyanov, *et al.*,²¹ reported the $E_{1/2}$ values for $\text{Fe}(\text{cp})(\text{biphenyl})^+$ and $\text{Fe}(\text{cp})(\text{fluorene})^+$ as -1.30 and -1.40 V vs. sce, respectively. The two-iron analogs each show two waves: $\text{Fe}_2(\text{cp})_2(\text{biphenyl})^{2+}$ at -1.17 and -1.27 V and $\text{Fe}_2(\text{cp})_2(\text{fluorene})^{2+}$ at -1.19 and -1.43 V. The first half-wave potential for $\text{Fe}^{\text{II}}\text{Fe}^{\text{I}} \rightarrow \text{Fe}^{\text{I}}\text{Fe}^{\text{I}}$ is the most changed in going to the two-iron species. A direct or ring-propagated Fe-Fe electron-exchange interaction would probably bear most heavily on the first oxidation wave in that it could stabilize the $\text{Fe}^{\text{II}}\text{Fe}^{\text{I}}$ species and thus move the first wave to more positive potentials. Comparison of the $\text{Fe}_2(\text{cp})_2(\text{biphenyl})^{2+}$ data with those for $\text{Fe}_2(\text{cp})_2(3,3',4,4'\text{-tetramethylbiphenyl})^{2+}$ is also enlightening. The electron-donating methyl substituents have caused a shift to more negative values of potential as expected from methylation. However, the shift for the second potential is greater than that for the first because the electron-exchange interaction is working to offset the methylation inductive effect.

Experimental Section

Compound Preparation. The general procedure for preparation of the various $[\text{Fe}_2(\text{cp})_2(\text{arene})](\text{PF}_6)_2$ and $[\text{Fe}(\text{cp})(\text{arene})](\text{PF}_6)$ compounds has been given in a previous paper.² All analyses were performed by the University of Illinois School of Chemical Sciences microanalytical laboratory; results for the compounds not reported in ref 2 are given in Table I. Most chemicals either were reagent grade or were purchased from commercial sources. Biferrrocene was prepared as reported,²⁴ phenylmesitylene was prepared by the standard diazotization method, and $[\text{Fe}(\text{HMBZ})_2](\text{PF}_6)_2$ was prepared as per Fischer, *et al.*²⁵

Physical Measurements. Electronic absorption spectra were recorded in Spectro-Grade acetonitrile with a Cary 14 spectrophotometer. Polarographic measurements were carried out with a Princeton Applied Research Model 174 polarograph. All measurements were performed on 10^{-3} M acetonitrile solutions with 0.1 M $((\text{C}_2\text{H}_5)_4\text{N})\text{ClO}_4$ electrolyte. Background corrections were made on all runs and all measurements were made at 25°. A dropping-mercury electrode was used; a rotating platinum electrode was tried and found to give poorly resolved nonreproducible waves. All solutions were thoroughly degassed before the runs. Constant-potential electrolyses were performed on a few compounds to check the n values obtained by comparison of limiting currents and in this work we used a PAR Model 175 galvanostat-potentiostat in conjunction with a standard three-compartment cell. A mercury pool working electrode and a platinum counterelectrode separated from the working compartment by a fine-porosity frit were used in all experiments. The saturated calomel electrode (sce) was connected *via* a salt bridge. The electrolyses were performed at the plateau of the particular wave being investigated. Iron-57 Mössbauer measurements were carried out on an apparatus described previously.²⁶

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Registry No. $[\text{Fe}(\text{HMBZ})_2](\text{PF}_6)_2$, 53382-63-1; $[\text{Fe}(\text{HMBZ})(\text{cp})](\text{PF}_6)$, 53702-66-2; $\text{Fe}(\text{benzene})(\text{cp})^+$, 51364-24-0; $[\text{Fe}(\text{chlorobenzene})(\text{cp})](\text{PF}_6)$, 33086-63-4; $\text{Fe}(\text{biphenyl})(\text{cp})^+$, 32758-65-9; $\text{Fe}(\text{naphthalene})(\text{cp})^+$, 46466-61-9; $\text{Fe}_2(\text{biphenyl})(\text{cp})_2^{2+}$, 51539-79-8; $\text{Fe}_2(\text{fluorene})(\text{cp})_2^{2+}$, 53730-29-3; $[\text{Fe}_2(\text{trans-stilbene})(\text{cp})_2](\text{PF}_6)_2$,

53746-36-4; $[\text{Fe}_2(1,1'\text{-binaphthyl})(\text{cp})_2](\text{PF}_6)_2$, 53849-10-8; $\text{Fe}_2(\text{chrysenes})(\text{cp})_2^{2+}$, 53702-63-9; $\text{Fe}_2(\text{anthracene})(\text{cp})_2^{2+}$, 53702-64-0; $\text{Fe}_2(\text{phenanthrene})(\text{cp})_2^{2+}$, 53702-65-1; $\text{Fe}(\text{cp})_2$, 102-54-5; $\text{Fe}_2(\text{pyrene})(\text{cp})_2^{2+}$, 53746-35-3; $\text{Fe}_2(1,2:4,5\text{-dibenzo-}1,4\text{-cycloheptadiene})(\text{cp})_2^{2+}$, 53276-64-5; $\text{Fe}_2(\text{biphenylmethane})(\text{cp})_2^{2+}$, 51539-80-1; $\text{Fe}_2(9,10\text{-dihydroanthracene})(\text{cp})_2^{2+}$, 53276-70-3; $[\text{Fe}_2(\text{phenylmesitylene})(\text{cp})_2](\text{PF}_6)_2$, 53746-33-1; $\text{Fe}_2(\beta\text{-phenylnaphthylene})(\text{cp})_2^{2+}$, 53746-34-2; $\text{Fe}_2(p\text{-terphenyl})(\text{cp})_2^{2+}$, 53276-66-7; $\text{Fe}_2(\text{bibenzyl})(\text{cp})_2^{2+}$, 53702-62-8; $\text{Fe}_2(3,3',4,4'\text{-tetramethylbiphenyl})(\text{cp})_2^{2+}$, 53702-60-6; $[\text{Fe}_2(\text{benzene})_2(\text{fulvalene})](\text{PF}_6)_2$, 53702-59-3.

References and Notes

- (1) Camille and Henry Dreyfus Fellow, 1972-1977.
- (2) W. H. Morrison, Jr., E. Y. Ho, and D. N. Hendrickson, *J. Amer. Chem. Soc.*, **96**, 3603 (1974).
- (3) Y. S. Sohn, D. N. Hendrickson, and H. B. Gray, *J. Amer. Chem. Soc.*, **93**, 3603 (1971).
- (4) N. Rösch and K. H. Johnson, *Chem. Phys. Lett.*, **24**, 179 (1974), and some seven references given therein of which a few are duplicated below for the arene citations.
- (5) E. M. Shustorovich and M. E. Dyatkina, *Dokl. Akad. Nauk SSSR*, **128**, 1234 (1959); **131**, 113 (1960); **133**, 141 (1960).
- (6) R. D. Fischer, *Theor. Chim. Acta*, **1**, 418 (1963).
- (7) R. Prins and F. J. Reinders, *Chem. Phys. Lett.*, **3**, 45 (1969).
- (8) I. H. Hillier and R. M. Canadine, *Discuss. Faraday Soc.*, **47**, 27 (1969).
- (9) M. F. Rettig and R. S. Drago, *J. Amer. Chem. Soc.*, **91**, 3432 (1969).
- (10) R. Prins, *J. Chem. Phys.*, **50**, 4804 (1969).
- (11) S. E. Anderson and R. S. Drago, *J. Amer. Chem. Soc.*, **91**, 3656 (1969).
- (12) S. E. Anderson and R. S. Drago, *Inorg. Chem.*, **11**, 1564 (1972).
- (13) D. O. Cowan, C. LeVanda, J. Park, and F. Kaufman, *Accounts Chem. Res.*, **6**, 1 (1973).
- (14) W. H. Morrison, Jr., S. Krogsrud, and D. N. Hendrickson, *Inorg. Chem.*, **12**, 1998 (1973).
- (15) W. H. Morrison, Jr., and D. N. Hendrickson, *J. Chem. Phys.*, **59**, 380 (1973).
- (16) W. H. Morrison, Jr., and D. N. Hendrickson, *Inorg. Chem.*, **13**, 2279 (1974).
- (17) W. H. Morrison, Jr., and D. N. Hendrickson, *Chem. Phys. Lett.*, **22**, 119 (1973).
- (18) D. R. Scott and F. A. Matsen, *J. Phys. Chem.*, **72**, 16 (1968).
- (19) R. A. Stukan, N. A. Vol'kenau, A. N. Nesmeyanov, and V. I. Gol'danskii, *Izv. Akad. Nauk SSSR, Ser. Khim.*, **8**, 1472 (1966).
- (20) A. N. Nesmeyanov, N. A. Vol'kenau, and E. I. Sirotkina, *Izv. Akad. Nauk SSSR, Ser. Khim.*, **5**, 1170 (1967).
- (21) A. N. Nesmeyanov, L. I. Denisovich, S. P. Gubin, N. A. Vol'kenau, E. I. Sirotkina, and I. N. Bolesova, *J. Organometal. Chem.*, **20**, 169 (1969).
- (22) I. U. Khand, P. L. Pauson, and W. E. Watts, *J. Chem. Soc. C*, 2257, 2261 (1968).
- (23) A. N. Nesmeyanov, N. A. Vol'kenau, L. S. Shiloviseva, and V. A. Petrakova, *J. Organometal. Chem.*, **61**, 329 (1973).
- (24) M. D. Rausch, *J. Org. Chem.*, **26**, 1802 (1961).
- (25) E. O. Fischer and F. Rohrscheid, *Z. Naturforsch. B*, **17**, 483 (1962).
- (26) E. Münck, P. G. Debrunner, J. C. M. Tsibris, and I. C. Gunsalus, *Biochemistry*, **11**, 855 (1972).

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Oxidation-State and Electron-Transfer Properties of Mixed-Valence 1,1'-Polyferrocene Ions

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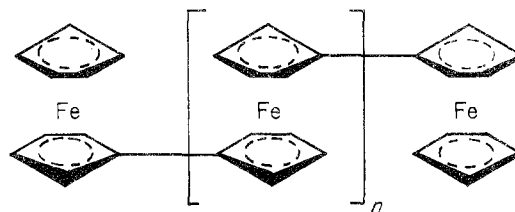
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The oxidation state properties of the compounds biferrocene, 1,1'-terferrocene, and 1,1'-quaterferrocene have been investigated using electrochemical techniques. In the polymeric compounds all of the ferrocene groups are oxidizable to ferricenium at distinct potentials. The values of the potentials can be predicted in some cases using ferrocenyl substituent effects. Partial oxidation gives a series of discrete mixed-valence ions. The mixed-valence ions can exist as a series of oxidation state isomers which differ with regard to the site of oxidation. Electron transfer between different oxidation state sites in the polymeric chains is unsymmetric giving energetically nonequivalent isomers. The unsymmetrical nature of electron transfer is reflected in the properties of intervalence-transfer (IT) absorptions in the near-infrared spectra. The existence of energetically equivalent and nonequivalent oxidation state isomers may also influence such properties as the intensities of IT bands, the presence of statistical effects in measured reduction potentials, and rates of intramolecular electron transfer.

Mixed-valence compounds which contain metal ions of the same element in different oxidation states are of considerable current interest.²⁻⁵ Cases in which the different oxidation state sites are held in close proximity either by the properties of a solid-state lattice or by a designed chemical linkage often have unusual physical properties. Commonly, such physical properties are unique to the mixed-valence material and not just the sum of the properties of the separate ions.

Detailed studies on the dimeric systems $(\text{NH}_3)_5\text{Ru}(\text{pyz})\text{-Ru}(\text{NH}_3)_5^{6+,5+,4+}$ (pyz is pyrazine)⁶⁻¹¹ and biferrocene,^{12,13} $(\text{C}_5\text{H}_5)\text{Fe}(\text{C}_5\text{H}_4\text{-C}_5\text{H}_4)\text{Fe}(\text{C}_5\text{H}_5)^{2+,+,0}$, have led to a considerable understanding of the extent and consequences of electronic interactions between metals in mixed-valence ions. In more extensively linked systems such as $(\text{bipy})_2\text{ClRu}(\text{pyz})[\text{Ru}(\text{bipy})_2\text{pyz}]_2\text{RuCl}(\text{bipy})_2^{10+,9+,8+,6+}$ (bipy is 2,2'-bipyridine)¹⁴ and $(\text{C}_5\text{H}_5)\text{Fe}(\text{C}_5\text{H}_4\text{-C}_5\text{H}_4)\text{Fe}(\text{C}_5\text{H}_4\text{-C}_5\text{H}_4)\text{-Fe}(\text{C}_5\text{H}_5)^{3+,2+,+,0}$ a series of mixed-valence ions can exist. Because of the possibility of cooperative interactions between more than two sites such mixed-valence systems may have physical properties intermediate between those of the simple dimers and mixed-valence solids. In this paper we report on the oxidation state and electron-transfer properties of the extensively linked 1,1'-polyferrocene compounds



biferrocene (Fc-Fc), $n = 0$

1,1'-terferrocene (Fc-Fc-Fc), $n = 1$

1,1'-quaterferrocene (Fc-Fc-Fc-Fc), $n = 2$

Experimental Section

Measurements. Visible and very near-infrared spectra were obtained using Cary Model 14 and 17 spectrophotometers. All electrochemical measurements were made at platinum electrodes vs. the saturated sodium chloride calomel electrode (ssce) at $24 \pm 2^\circ$ and are uncorrected for junction potentials. In all electrochemical experiments, standard three-electrode operational amplifier circuitry was used as previously described.¹⁵ Values of n , where n is the total number of electrons transferred in exhaustive electrolysis at constant potential, were calculated after measuring the total area under current vs. time curves for the complete reaction. Reactions were judged to be complete when the current had fallen below 1% of its initial value.