

31.6, 38.2, 39.6, 68.8, and 69.8 (C-8), 99.1 and 99.5 (C-4), 144.2 and 145.8 (C-3). The NMR spectra clearly indicated the presence of roughly equal amounts of the two expected⁵ isomers. A small portion was sublimed at 35 °C (at 10⁻³ mmHg) as orange needles: IR (cyclohexane) 2051, 1991 1965 cm⁻¹, (Nujol) 1074, 1030, 940, 921, 879 cm⁻¹; *m/z* 292 (1%, M⁺), 264, 137, 123, 109, 95, 82, 81, 67. Anal. Calcd for C₁₃H₁₄O₄Fe: C, 53.4; H, 5.5. Found: C, 53.3; H, 5.6.

Acknowledgment. We thank Syntex Research, Palo Alto, CA, for a generous gift of (-)-3β-(acetyloxy)pregna-5,6-dien-20-one.

Registry No. 1, 89-82-7; 2, 34413-88-2; 3, 979-02-2; 4, 16161-84-5; 5, 36065-09-5; 6, 984-84-9; 7a (isomer 1), 74242-51-6; 7a (isomer 2), 74242-47-0; 7b (isomer 1), 74242-50-5; 7b (isomer 2), 74242-90-3; 7c (isomer 1), 90129-93-4; 7c (isomer 2), 90129-94-5; 8a (isomer 1), 74219-69-5; 8a (isomer 2), 90129-95-6; 9a, 20023-36-3; 9b, 2886-59-1; Fe(CO)₅, 13463-40-6; Fe₂(CO)₉, 15321-51-4; (-)-myrtenal, 564-94-3; 1-methoxy-1,4-cyclohexadiene, 2886-59-1; chlorotris(triphenylphosphine)rhodium, 14694-95-2; 1-methoxy-4-methyl-1,4-cyclohexadiene, 20023-36-3; β-pinene, 127-91-3; methyl 2,4-hexadienoate, 1515-80-6; ((+)-pulegone)tricarbonyliron (isomer 1), 90129-96-7; ((+)-pulegone)tricarbonyliron (isomer 2), 90129-97-8.

An Electrochemical Study of the Reduction of Mono- and Bis(iron) Cyclophane Complexes

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The electrochemical reduction of six [(η⁵-C₅H₅)Fe(η⁶-cyclophane)]⁺PF₆⁻ and four [(η⁵-C₅H₅)Fe]₂(cyclophane)]²⁺(PF₆)₂²⁻ complexes were studied in several aprotic solvents by cyclic voltammetry, polarography, chronoamperometry, and coulometry. The mono(iron) complexes reduce in two one-electron steps (+/0/-) separated by 0.6–0.8 V. The neutral radical complexes are less stable than other CpFe(arene) radicals. Ease of reduction and stability of the neutral radicals seems to depend on the extent of overlap of metal and ligand orbitals. The bis(iron) complexes reduce in two one-electron steps (2+ / +/0) separated by 0.15–0.25 V, depending on cyclophane structure and solvent. This is interpreted as sequential reduction of each iron with the extent of the Fe–Fe interaction affecting the potential separation. Decomposition of the reduced mono- and bis(iron) complexes proceeds by loss of the cyclophane followed by disproportionation of the CpFe^I fragment to ferrocene and Fe(0).

The chemical and electrochemical reductions of the mixed-sandwich cations [(η⁵-C₅H₅)Fe(η⁶-C₆R₆)]⁺ have been extensively studied,²⁻⁹ and a variety of the corresponding CpFe(arene) neutral radicals have been shown to be quite stable.⁵⁻⁹ Under the proper conditions, though, they may undergo dimerization or other radical reactions.

Initial polarographic investigations³ of these compounds in acetonitrile established that the complexes underwent two one-electron reductions; only the first was found to be reversible. Shortly thereafter, the nominally Fe(I) neutral radical was isolated.⁴ The potential of the first reduction varied with the substituents on the arene ring and ranged from -1.0 to -1.5 V vs. SCE. Because the stability of the radical depended upon the solvent, dis-

placement of the arene was assumed to be the pathway of decomposition to ferrocene and free arene.

More recently the reactivity of these radicals and their second one-electron reduction have been extensively investigated. Nesmeyanov et al.⁵ reported electrochemical detection of a significant lifetime for [CpFe(naphthalene)]⁻, and El Murr⁶ reported cyclic voltammetry studies showing that the second reduction of CpFe(benzene)^{0/-} is chemically reversible in THF. In the presence of electrophiles, the anions suffer attack at the arene to form neutral cyclohexadienyl complexes.

Astruc and co-workers⁷⁻⁹ investigated in detail the redox chemistry of the complexes [(η⁵-C₅H_{5-*m*}R_{*m*})Fe(η⁶-C₆H_{6-*n*}R_{*n*})]⁺ (R = Me, Et; *m* = 0–5; *n* = 0–6). The stability of the generally persistent radicals, as well as reaction pathway, depended on alkyl substitution. In aprotic solvents dimerization of some of the radicals occurred through the arene ring; others underwent loss of the arene followed by disproportionation to ferrocene.^{7,9} Because of the stability and low redox potential (-1.6 to -1.9 V vs. SCE in aqueous 0.1 M LiOH),⁸ these 19-electron complexes make useful reducing agents.^{8,9}

Hendrickson et al.¹⁰ investigated the electrochemistry of a variety of novel [(CpFe)₂(arene)]²⁺ complexes in which each CpFe fragment is bonded to different centers in

- (1) (a) University of Vermont. (b) University of Oregon.
 (2) Nesmeyanov, A. N.; Vol'kenau, N. A.; Shilovtseva, L. S. *Dokl. Akad. Nauk SSSR* 1970, 190, 354.
 (3) Nesmeyanov, A. N.; Denisovich, L. I.; Gubin, S. P.; Vol'Kenau, N. A.; Sirotkina, E. I.; Boleseva, I. N. *J. Organomet. Chem.* 1969, 20, 169.
 (4) Nesmeyanov, A. N.; Vol'Kenau, N. A.; Shilovtseva, L. S.; Petrakova, V. A. *J. Organomet. Chem.* 1973, 61, 329.
 (5) Nesmeyanov, A. N.; Vol'Kenau, N. A.; Petrovskii, P. V.; Kotova, L. S.; Petrakova, V. A.; Denisovich, L. T. *J. Organomet. Chem.* 1981, 210, 103.
 (6) El Murr, N. *J. Chem. Soc., Chem. Commun.* 1981, 251.
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 (8) Hamon, J. R.; Astruc, D.; Michaud, P. *J. Am. Chem. Soc.* 1981, 103, 758.
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- (10) Morrison, W. H., Jr.; Ho, E. Y.; Hendrickson, D. N. *J. Am. Chem. Soc.* 1974, 96, 3603. Morrison, W. H.; Ho, E. Y.; Hendrickson, D. N. *Inorg. Chem.* 1975, 14, 500.

polyaromatic ligands. Each iron reduced separately by one electron, indicating that there was significant electronic interaction between the two iron atoms (either through space or through the rings). The potential separation between the first and second reductions was taken as a measure of the electron interaction between the two irons,¹⁰ on the basis that a greater interaction will give rise to a greater potential separation.

This paper reports our electrochemical investigation of a variety of $[(\text{CpFe}(\eta^6\text{-cyclophane}))]^+$ and $[(\text{CpFe})_2(\text{cyclophane})]^{2+}$ complexes. Because the principal mode of reaction of the neutral $\text{CpFe}(\text{arene})$ radicals is dimerization through the arene and of $[\text{CpFe}(\text{arene})]^-$ is protonation of the arene, we hoped that the cyclophane ligands would be inert to these pathways and so provide more stable neutral and anionic complexes. Furthermore, the redox properties of the cyclophane complexes were seen as a probe to a better understanding of the differences between the physical and chemical properties of cyclophane and normal arene π complexes.

Cyclophane ligands can coordinate two CpFe moieties, one to each benzene deck in the ligand (e.g., complexes 7–10),^{11–16} and investigation of the redox properties of these bis(iron) systems gives information about the interaction between the two metal redox centers. Knowledge of this interaction is important in designing polymeric structures which, because of the demonstrated transannular interaction between the two benzene decks, might provide a one-dimensional conductor.^{14,15}

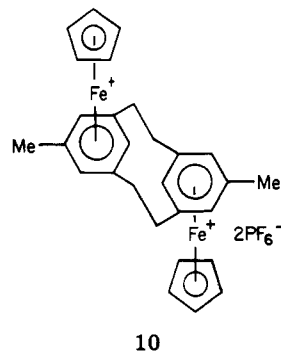
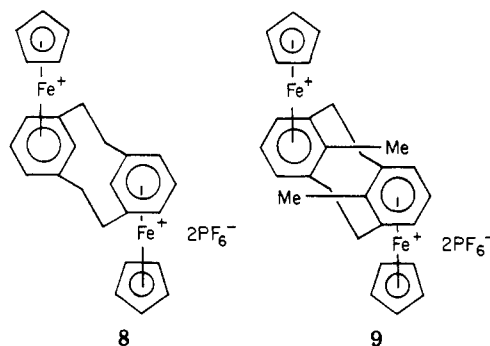
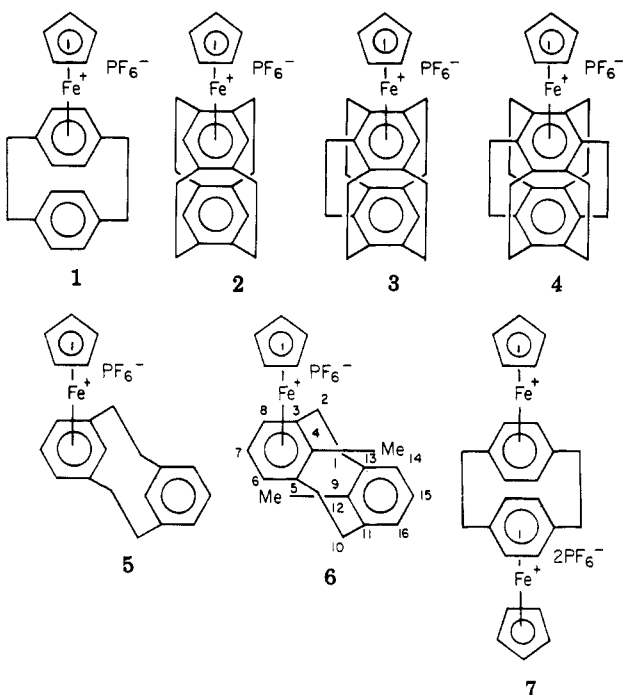
Previous work on the electrochemistry of metal-cyclophane complexes is limited to the work of Finke, Boekelheide, et al.,^{15,16} who investigated $[(\eta^6\text{-C}_6\text{Me}_6)\text{Ru}(\eta^6\text{-cyclophane})]^{2+}$ complexes. These complexes reduce by two electrons, and the neutral complexes isomerize to $(\eta^4\text{-arene})\text{Ru}^0$ complexes. The ease with which the cyclophane assumed the η^4 configuration was related to the $E_{1/2}$ values.

We have now investigated the electrochemical reduction of six $[\text{CpFe}(\text{cyclophane})]^+$ complexes (compounds 1–6) and four $[(\text{CpFe})_2(\text{cyclophane})]^{2+}$ complexes (compounds 7–10).¹⁶ These complexes were studied by cyclic voltammetry, polarography, chronoamperometry, and controlled potential coulometry in a variety of organic solvents.

Experimental Section

The preparations of compounds 1 and 7 have been described previously by Laganis et al.,¹² compounds 5, 6, 8, and 9 by Swann and Boekelheide,¹³ and compound 10 by Koray.¹⁴ Compounds 2, 3, and 4 were prepared following the same procedure given previously for 1,¹² and the details of their preparation and characterization follow.

(η^5 -Cyclopentadienyl)(η^6 -[2₄](1,2,4,5)cyclophane)iron(II) hexafluorophosphate (2) was isolated in 96% yield after recrystallization from a dichloromethane-tetrahydrofuran mixture as reddish orange crystals: mp >220 °C dec; ¹H NMR ($\text{CD}_3\text{C}(\text{=O})\text{CD}_3$) δ 6.43 (2 H, s, ArH), 5.49 (2 H, s, ArH), 4.82 (5 H, s, CpH), 3.56–2.61 (16 H, m, CH₂). Anal. Calcd for $\text{C}_{25}\text{H}_{25}\text{F}_6\text{FeP}$: C, 57.06; H, 4.79. Found: C, 56.81; H, 4.38.



(η^5 -Cyclopentadienyl)(η^6 -[2₅](1,2,3,4,5)cyclophane)iron(II) hexafluorophosphate (3) was isolated in 83% yield after recrystallization from acetone by slow ether diffusion to give reddish orange crystals: mp >220 °C dec; ¹H NMR ($\text{CD}_3\text{O}(\text{=O})\text{CD}_3$) δ 6.32 (1 H, s, ArH), 5.10 (1 H, s, ArH), 4.79 (5 H, s, CpH), 3.50–2.42 (20 H, m, CH₂). Anal. Calcd for $\text{C}_{27}\text{H}_{27}\text{F}_6\text{FeP}$: C, 58.71; H, 4.93. Found: C, 58.61; H, 4.64.

(η^5 -Cyclopentadienyl)(η^6 -[2₆](1,2,3,4,5,6)cyclophane)iron(II) hexafluorophosphate (4) was isolated in 62% yield after precipitation from nitromethane by addition of ether to give a pink solid: mp >220 °C dec; ¹H NMR ($\text{CD}_3\text{C}(\text{=O})\text{CD}_3$) δ 4.76 (5 H, s, CpH), 3.20 (24 H, br s, CH₂). Anal. Calcd for $\text{C}_{29}\text{H}_{29}\text{F}_6\text{FeP}\cdot 2\text{H}_2\text{O}$: C, 56.70; H, 5.42. Found: C, 57.18; H, 5.69.

Ferrocene (Strem Chemicals) was used as received. Tetra-*n*-butylammonium hexafluorophosphate (TBAHFP) was prepared by metathesis of Bu_4NI and NH_4PF_6 in acetone/water, recrystallized three times from 95% ethanol, and dried under vacuum at 100 °C for 24 h. Tetra-*n*-butylammonium tetrafluoroborate (Pfaltz and Bauer) was recrystallized from 95% ethanol three

(11) Laganis, E. D.; Finke, R. G.; Boekelheide, V. *Tetrahedron Lett.* 1980, 21, 4405.

(12) Laganis, E. D.; Finke, R. G.; Boekelheide, V. *Proc. Natl. Acad. Sci. U.S.A.* 1981, 78, 2657.

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(14) Koray, A. R. *J. Organomet. Chem.* 1981, 212, 233; 1982, 232, 345.

(15) Laganis, E. D.; Voegeli, R. H.; Swann, R. T.; Finke, R. G.; Hopf, H.; Boekelheide, V. *Organometallics* 1982, 1, 1415.

(16) Finke, R. G.; Voegeli, R. H.; Laganis, E. D.; Boekelheide, V. *Organometallics* 1983, 2, 347.

(17) The naming and numbering of these cyclophane complexes follows a procedure suggested previously (Boekelheide, V. *Top. Curr. Chem.* 1983, 113, 87).

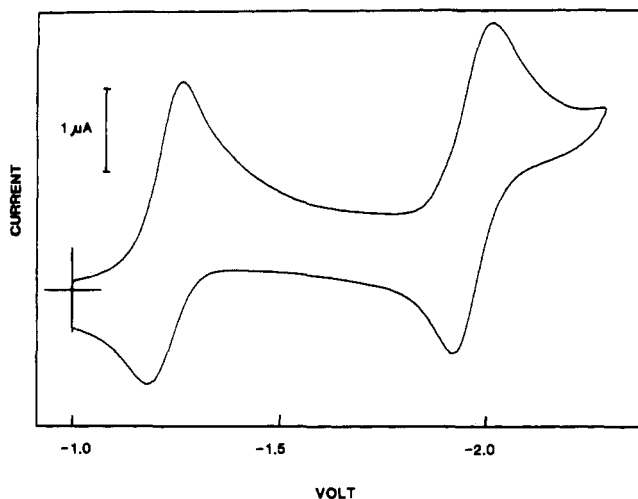


Figure 1. Cyclic voltammogram of 1 in THF/0.1 M TBAHFP on an HMDE (scan rate = 0.2 V/s).

times and dried under vacuum at 100 °C for 24 h.

N,N-dimethylformamide (DMF), acetone, and acetonitrile (CH_3CN) (Burdick and Jackson) were dried over Type 4A molecular sieves. Tetrahydrofuran (THF) (Aldrich Gold Label) was distilled from Na/benzophenone, and methylene chloride (Burdick and Jackson) was distilled from CaH_2 immediately before use.

Voltammetry was performed under nitrogen. A three-electrode cell was used with the saturated calomel reference electrode (SCE) segregated from the test solution by a fine frit. The platinum bead electrode was pretreated by placing it in the vapor of refluxing nitric acid (5 min) followed by immersion in saturated aqueous ferrous ammonium sulfate and rinsing with distilled water. Triply distilled mercury from Bethlehem Apparatus, Co., was used for the hanging mercury drop electrode (HMDE) and dropping mercury electrode (DME). Bulk electrolyses were performed in a nitrogen-filled Vacuum Atmosphere Co. drybox, Model No HE-493. Electrochemical instrumentation was PARC equipment and ancillary devices described previously.^{18,19}

Analysis of free $[\text{2}_2](1,4)$ cyclophane after bulk electrolysis was done by evaporation of the acetone followed by dissolving the entire residue in acetonitrile. Then, the $[\text{2}_2](1,4)$ cyclophane was identified by its oxidative peak potential²⁰ and measured by its peak current compared to the original complex (by cyclic voltammetry).

The computer simulator is described by Feldberg.²¹ The simulations were executed on a DEC 2060 running under the TOPS 20 operating system. Electron spin resonance spectra were obtained with a Varian V-4502 spectrometer using frozen solutions at -130 °C. Spectra were calibrated with DPPH by using a dual-cavity arrangement.

Results

General Redox Behavior. In THF and CH_2Cl_2 , all of the $[\text{CpFe}(\text{cyclophane})]^+$ complexes reduced by one electron between -0.9 and -1.5 V vs. SCE. With cyclic voltammetry, the reduction was quasi-reversible ($\Delta E_p = 60\text{--}80$ mV at 0.1 V/s)¹⁹ for all of the complexes except 4. In THF and acetone, all of the mono(iron) complexes underwent a second reduction 0.6–0.8 V negative of the first excepting 3 and 4 (see Table Ia and Figure 1). The second reduction, when characterized, was shown to involve an ECE mechanism.²² Bulk electrolysis of 1 at the first reduction po-

Table I. Cyclic Voltammetry Data of Mono- and Bis(iron) Complexes (Acetone/0.1 M TBAHFP, Potentials vs. SCE, and a Pt Bead)

a. Mono(iron) Complexes					
compd	E_{p1} , V	E_{p2} , V	ΔE_{p1} , ^c mV	ΔE_{p2} , ^c mV	i_{pa}/i_{pc} ^c
1	-1.34	-2.02	60	76	0.77
2	-1.06	-1.84	64	70	0.95
3 ^a	-1.08	b	80	b	0.76
4 ^a	-1.34	b			0.0
5	-1.43	-2.08	68	110	0.84
6	-1.35	-1.98	80	95	0.83
b. Bis(iron) Complexes					
compd	E_{p1} , V	E_{p2} , V	ΔE_{p1} , ^c V	ΔE_{p2} , ^c V	$E_{p1} - E_{p2}$, mV
77	-1.18	-1.32	70	d	140
88	-1.24	-1.40	62	82	160
99	-1.16	-1.37	65	72	210
10	-1.28	-1.42	62	80	140

^a Potential measured in CH_2Cl_2 because compound did not give clean electrochemistry in acetone. Potentials between acetone and CH_2Cl_2 corresponded to within 10 mV for other compounds. ^b See Discussion. ^c At 0.10 V/s = v. ^d Return current insufficient to determine.

tential passed one electron; ferrocene and free $[\text{2}_2](1,4)$ -cyclophane were the major products. Electrolysis of 2 by one electron generated the neutral radical complex that was relatively persistent.

Electrochemistry of the bis(iron) complexes was not always reproducible. Although voltammetry at the hanging mercury drop electrode (HMDE) was far worse than the platinum bead electrode, at both electrodes misshapen and spurious peaks were observed following either stirring of solution or scanning negative of the reductions. No reproducible scans were obtained on a single mercury drop, but cyclic voltammograms could be reproduced on a Pt bead by wiping the electrode after each scan. Furthermore, although potentials of a ferrocene standard were quite reproducible (± 2 mV in acetone), peak potentials for 7 varied by as much as 20 mV from one experiment to another. Other bis(iron) complexes were more reproducible (± 10 mV). The potentials reported are the average of a number of experiments.

The bis(iron) complexes all underwent two one-electron reductions between -1.0 and -1.4 V vs. SCE. The separations between E_{p2} and E_{p1} were from 140 to 250 mV (see Table Ib). Peak separation depended on solvent, supporting electrolyte, and cyclophane. A third reduction occurred at about -2.0 V for all bis(iron) complexes but was not extensively characterized because of severe electrode fouling. Bulk electrolysis negative of the first two reductions passed two electrons and also produced ferrocene and free cyclophane.

Because 1, 7, and 10 were available in the largest quantities, these complexes were studied in the greatest depth. The other complexes behaved similarly; significant differences are noted.

$[\text{CpFe}([\text{2}_2](1,4)\text{cyclophane})]^+$, 1. In acetone, dc polarography showed that the first reduction of 1 is reversible [slope of E vs. $\log(i/i_d - i) = -0.063$ V], one electron, and is diffusion controlled (plot of i_d vs. (column height)^{1/2} linear through origin). Cyclic voltammetry suggested these same conclusions with $\Delta E_p = 60$ mV (at $v = 0.1$ V/s) and

(18) Moraczewski, J.; Geiger, W. E., Jr. *J. Am. Chem. Soc.* 1981, 103, 4779.

(19) v = scan rate (cyclic voltammetry); i_p = peak current (cyclic voltammetry); E = potential; E_p = peak potential (cyclic voltammetry); ΔE_p = potential separation between anodic and cathodic peaks; I = diffusion current constant ($\mu\text{A s}^{-1/2} \text{mg}^{-2/3} \text{mM}^{-1}$); i_a/i_c = ratio of peak anodic and cathodic currents (cyclic voltammetry); $L_p/v^{1/2}$ = current function of cyclic voltammetry.

(20) Sato, T.; Torizuka, K. *J. Chem. Soc., Perkin Trans. 2* 1978, 1199.

(21) Feldberg, S. W. *Electroanal. Chem.* 1969, 3, 199.

(22) E = electrochemical step; C = chemical step. ECE is the notation for a mechanism whereby an electron transfer causes a chemical step that then results in another electron transfer (e.g., $\text{A}^+ + e^- \xrightarrow{\text{E}} \text{A} \xrightarrow{\text{C}} \text{B} + e^- \xrightarrow{\text{E}} \text{B}^-$).

$i_p/v^{1/2}$ constant. The reactivity of the neutral radical is indicated by the lack of complete chemical reversibility at $v = 0.1$ V/s ($i_a/i_c = 0.69$).

In DMF, the reduction is slightly less chemically reversible than in less strongly coordinating solvents ($i_a/i_c = 0.60$ at $v = 0.1$ V/s), and in acetonitrile it is completely irreversible at $v = 0.1$ V/s.

The partial chemical reversibility of the second reduction is indicated by cyclic voltammetry: $i_a/i_c = 0.64$ and $\Delta E_p = 75$ mV at $v = 0.1$ V/s in acetone, meaning that the monoanion $[\text{CpFe}([2_2](1,4)\text{cyclophane})]^-$ has a lifetime only slightly shorter than that of the neutral radical.

Other $[\text{CpFe}(\text{cyclophane})]^+$ Complexes 2–6. Most other mono(iron) cyclophane complexes behaved similarly to 1, varying only slightly in the reversibility and potential of the couples (Table Ia). Compounds 3 and 4 were exceptions.

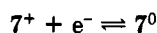
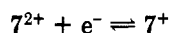
The first reduction of 3 was quasi-reversible and diffusion controlled like 1 ($E_p = -1.26$ V). However, on an HMDE, cyclic voltammetry showed two more waves. The first of these was apparently due to electrode product adsorption (i_p/v constant), and the peak potential was quite dependent on scan rate ($E_p = -2.05$ at $v = 0.2$ V/s). Characterization of the third wave was interfered with by the adsorption wave but appeared to be a one-electron (in comparison with first wave), diffusion-controlled, chemically irreversible reduction ($E_p = -2.15$ V).

The electrochemistry of 4 was surprising in that it had one irreversible reduction. At -50 °C in THF, cyclic voltammetry on a Pt bead at 0.75 V/s gave no evidence for a radical of significant lifetime.

$[(\text{CpFe})_2([2_2](1,4)\text{cyclophane})]^{2+}$, 7. Complex 7 underwent two reductions: $E_{p1} = -1.18$ V and $E_{p2} = -1.32$ V (cyclic voltammetry on a Pt bead at 0.1 V/s in acetone, Figure 2a). The peak separation of the forward and reverse scan of the first reduction (2+/+) is about 70 mV. Dc polarography indicates a less reversible reduction, but this is likely an effect of the mercury electrode. The peak separation in the cyclic voltammogram of the second reduction (+/0) could not be measured, but in this case dc polarography indicated that it was electrochemically reversible (polarographic slope is 0.060 V).

Diffusion control and reversibility were demonstrated for the first reduction by cyclic voltammetry (constant $i_p/v^{1/2}$ and peak potential from 0.015 to 0.50 V/s). The peak current of the second reduction (measured by extrapolation of the current decay of the first reduction) was equal to that of the first reduction and was diffusion controlled. Furthermore, chronoamperometry negative of the second reduction suggested overall diffusion control (constant $it^{1/2}$).

Computer simulation of the reductions supports a diffusion-controlled EE mechanism as well.



Comparison of experimental and theoretical cyclic voltammogram curves gave very good agreement on the negative (cathodic) scan. A lack of complete agreement on the anodic curve can be explained by electrode fouling and a lack of complete chemical reversibility of the two reductions. In Figure 2, a cyclic voltammogram of 7 in $\text{CH}_2\text{Cl}_2/0.1$ M TBAHFP is compared with EE and EEC simulations. In Figure 3, the cyclic voltammogram of 8 in acetone/ 0.1 M TBAHFP agrees very well with the EE simulation on the forward and reverse scan. It can be seen that the second reduction of 8 is nearly chemically reversible. Although not pictured, simulations of the cyclic

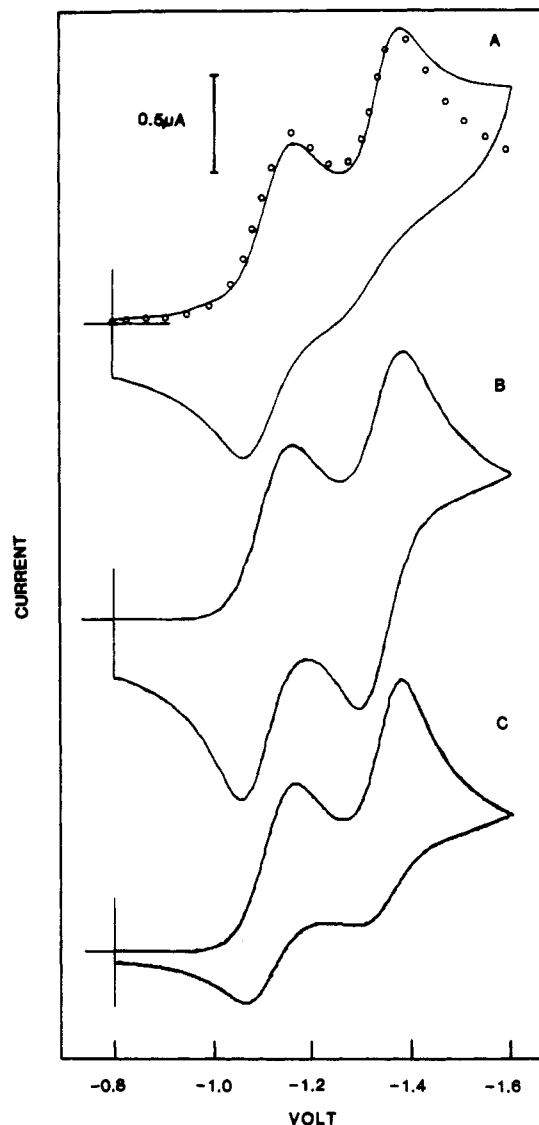


Figure 2. A. Cyclic voltammogram (—) of 7 in $\text{CH}_2\text{Cl}_2/0.1$ M TBAHFP on a platinum bead electrode (scan rate = 0.3 V/s). Computer simulation (O) of cathodic scan added to experimental charging current, EE mechanism. B. Computer-simulated cyclic voltammogram, EE mechanism. C. Computer-simulated cyclic voltammogram, EEC mechanism.

voltammetry of 7 in acetone/ 0.1 M TBAHFP ($v = 0.20$ and 0.05 V/s) and in acetone/ 0.1 M TBATFB also gave very good agreement with an EE mechanism.

Therefore, the computer simulations support the conclusion that the two waves represent an EE mechanism with less than complete chemical reversibility of the second reduction. This evidence, along with similar results of Hendrickson et al.¹⁰ points rather conclusively to sequential reductions of each iron.



The bis(iron) *anti*- $[2_2](1,3)$ cyclophane complexes 8, 9, and 10 behaved similarly to 7 with the exceptions that i_{p2}/i_{p1} ratios tended to be larger and the apparent chemical reversibility of the second reduction was significantly greater for these complexes (vide infra).

Bulk Electrolyses. Bulk electrolysis of 1 in acetone/ 0.1 M TBAHFP at -15 °C passed 1.03 electrons ($E = -1.6$ V vs. SCE). Electrolysis at room temperature required 1.22 electrons and produced ferrocene (78% of theoretical yield, Scheme I) and free $[2_2](1,4)$ cyclophane (quantitatively) as measured by cyclic voltammetry peak

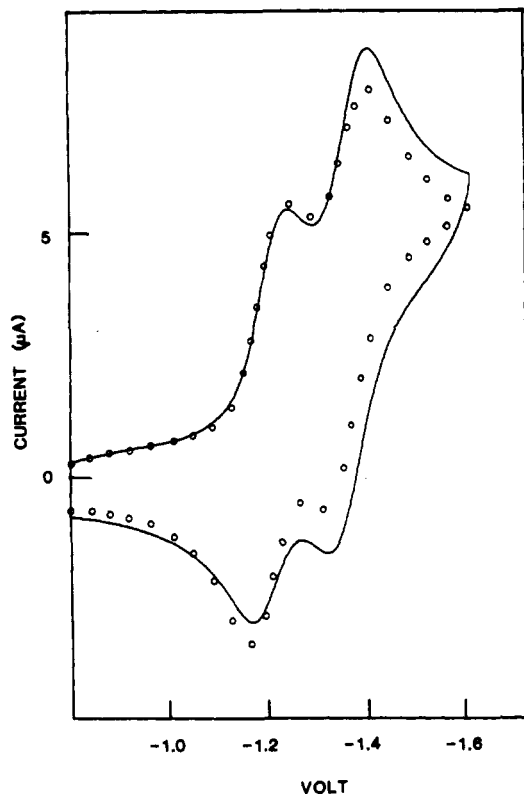


Figure 3. Cyclic voltammogram of 8 in acetone/0.1 M TBAHFP on a platinum bead electrode (scan rate = 0.2 V/s). Computer-simulated cyclic voltammogram (O), EE mechanism.

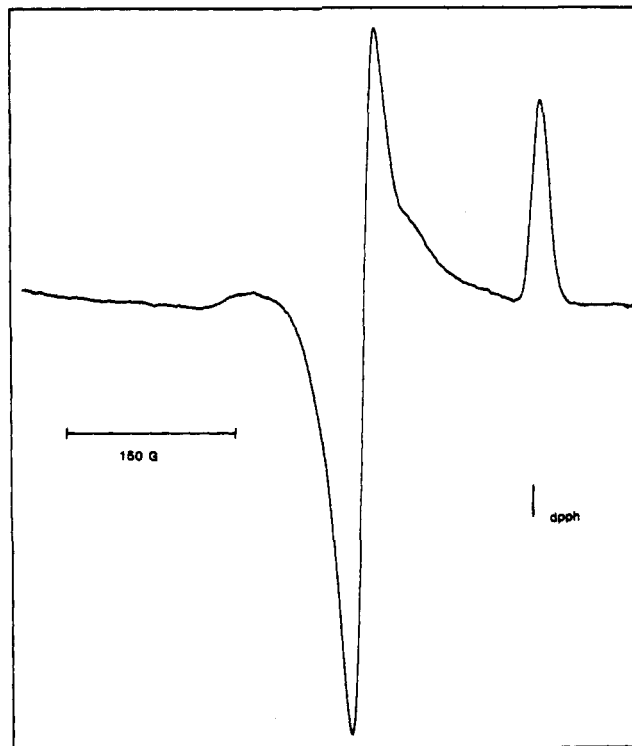
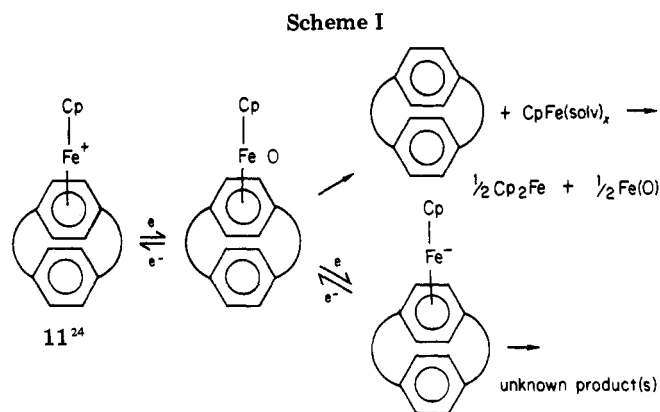


Figure 4. ESR spectrum of neutral 2 in frozen acetone at ca. 140 K.



currents assuming equal diffusion coefficients.

A bulk electrolysis of 2 was performed because, in contrast to 1, the cyclic voltammograms of 2 showed complete chemical reversibility in acetone and acetonitrile at room temperature. At -20°C an exhaustive electrolysis of 2 in acetone at -1.4 V quantitatively generated the neutral complex (detected by the rotating platinum electrode). In contrast with the deep green colors of $[\text{CpFe(arene)}]$,⁸ the neutral radical of 2 is light pink. Its frozen solution ESR spectrum (see Figure 4) is similar in a gross sense to those seen for other CpFe(arene) complexes.²³ Spectra of mixed-sandwich complexes such as $\text{CpFe}(\text{C}_6\text{Me}_6)$ display rhombic g tensors, but the g_x and g_y components are close enough to be treated as g_{\perp} in calculations, and the criterion $g_{\perp} > g_{\parallel}$ was used to identify the Fe(I) oxidation state in these complexes. Complex 2 has an axially symmetric spectrum with $g_{\perp} = 2.102$ and $g_{\parallel} = 1.997$, consistent with an Fe(I) formulation for the neutral π -complex radical.

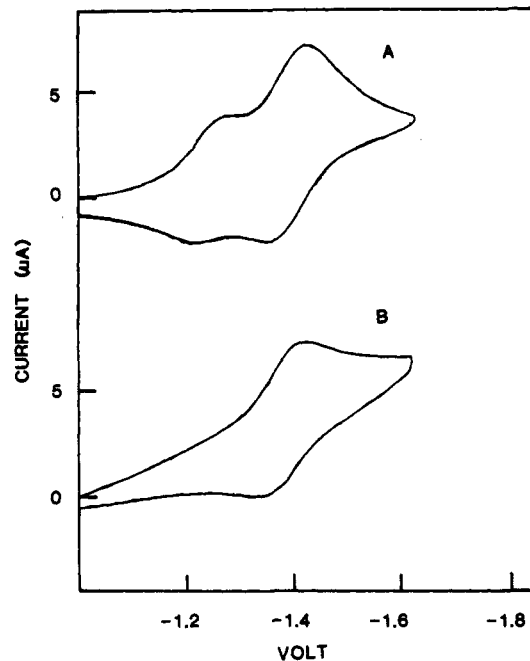


Figure 5. A. Cyclic voltammogram of 10 in acetone/0.1 M TBAHFP on a platinum bead electrode (scan rate = 0.12 V/s). B. Cyclic voltammogram after electrolysis by four electrons at -1.25 V (scan rate = 0.12 V/s).

When slowly warmed to room temperature, the cation was regenerated completely.

Bulk electrolysis of 7 at -1.5 V in acetone at room temperature passed an average of 2.04 electrons (six trials) and gave ferrocene in yields between 35% and 65% when analyzed; $[2_2](1,4)$ cyclophane was liberated quantitatively.

An electrolysis of 10, 20 mV positive of the peak potential of the first reduction (to generate only the singly reduced species), underwent regeneration as indicated by an increasing $i_{\text{electrolysis}} t^{1/2}$. Electrolysis was discontinued after four electrons were passed. Cyclic voltammetry after electrolysis showed a single wave at the same potential as

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the initial E_{p2} (see Figure 5); only a small amount of ferrocene was generated.

Discussion

Similar to other CpFe(arene) cation complexes, 1-6 show two reductions. The first wave is a one-electron reversible reduction, and in contrast to other CpFe(arene) complexes,⁶ the second reduction is an EC or an ECE process.

Although the neutral complexes are unstable, decomposition products are not generally observed on the cyclic voltammetry time scale in THF or acetone. Thus, the first decomposition product A is not electroactive in the potential range scanned. As discussed by Nesmeyanov et al.,³ A is probably a solvated CpFe^I fragment resulting from solvent displacement of the cyclophane. This fragment can then either decompose by undetermined pathways or can disproportionate to ferrocene and Fe(0) or an Fe(0) complex (see Scheme I).

A similar overall mechanism is also likely for the bis(iron) complexes. The lack of complete chemical reversibility of the first reduction is probably due to loss of the reduced CpFe(I) fragment much like that of the mono(iron) complexes. This decomposition should not affect the current magnitude of the second reduction because the time scale of the cyclic voltammetry experiment is too short. Furthermore, even if the decomposition were fast, in all cases the mono(iron) complex (which remains after loss of the CpFe fragment) reduces within 30 mV of the second reduction of its bis(iron) analogue. Presumably, neutral (CpFe)₂(cyclophane) also will decompose to neutral (CpFe)(cyclophane) that then can decompose further as discussed above. The neutral (CpFe)₂(cyclophane) complex will oxidize on the return scan causing the second reduction to appear more reversible than it really is. That the second wave appears more chemically reversible than the first is demonstrated qualitatively by cyclic voltammetry (visually comparing the two return waves and comparison to computer simulation) and quantitatively by reverse pulse polarography of the *anti*-[2₂](1,3)cyclophane complexes 8-10.

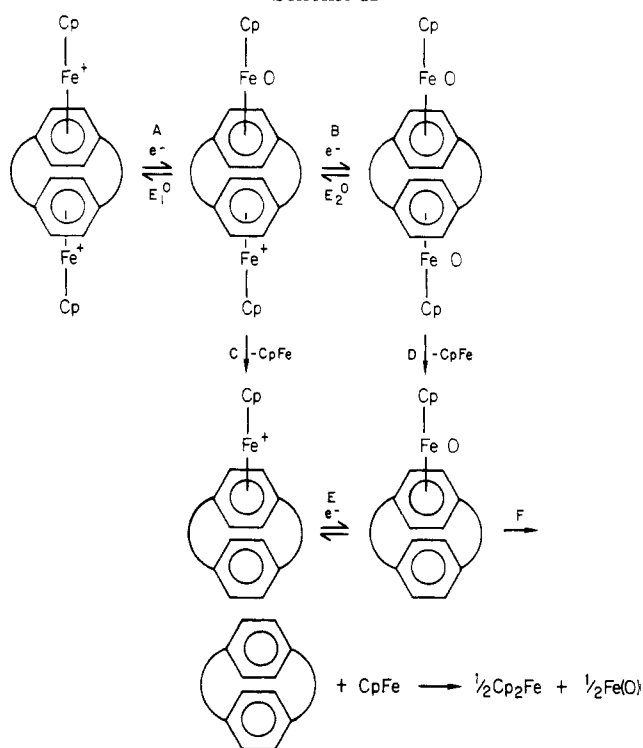
Thus, Scheme II can be proposed for the bis(iron) complexes. Evidence for pathway C is derived from that parallel with Scheme I, the less than complete reversibility of redox couple A ($i_a/i_c = 0.5$ at -30°C , $v = 0.75$ V/s, 7), and, most importantly, a bulk electrolysis of 10 at the first reduction potential. This electrolysis resulted in a single wave at the same potential as the original second wave (attributed to the mono(iron) analogue). B is included because of partial stability of the singly reduced species as well as the constant potential and current function of the waves at varying scan rates. D is proposed because of the coincidence of the potentials (as demonstrated by independent measurements) of B and D. Finally, E is proposed because of the larger apparent reversibility of the second reduction than the first as well as because of its consistency with other proposed chemical steps in Schemes I and II.

The relative importance of reactions B, C, D, E, and F is dependent upon compound and solvent. Figure 2 suggests a predominantly EEC mechanism for 7 in CH₂Cl₂ (important steps are A, B, E, and F); Figure 3 supports an EE mechanism for 8 in acetone (steps A and B); Figure 5 suggests an ECE mechanism for 10 in acetone (important steps are A, C, and D).

Stability of the CpFe(cyclophane) Radicals. Two trends in the data on radical stability are surprising. First,

(24) The cyclophane moiety shown in structure 11, as well as elsewhere, is a generalized structure intended to represent any one of the possible [2_n]cyclophanes.

Scheme II



most CpFe(cyclophane) radicals are less stable than CpFe(arene) radicals. Secondly, the radical stability can change greatly with relatively small changes in cyclophane structure. (The half-life of the radical derived from 2 is at least 4 orders of magnitude longer than that derived from 4: $t_{1/2}^{(2)} > 30$ min and $t_{1/2}^{(4)} < 0.3$ s).

Elschenbroich et al.²⁵ attributed the instability of $(\eta^6\text{-}[2_2](1,4)\text{cyclophane})_2\text{Cr}^+$ relative to $(\eta^6\text{-}p\text{-xylene})_2\text{Cr}^+$ to the convexity of the cyclophane, arguing that the cyclophane structure exposes the chromium center to solvent attack. Similarly, the increased stability of $(\eta^{12}\text{-}[2_2](1,4)\text{cyclophane})\text{Cr}^+$ relative to $(\eta^6\text{-}p\text{-xylene})\text{Cr}^+$ was attributed to the concavity of the coordinated rings shielding the metal, as well as to the chelating nature of this coordination.²⁵

However, this does not explain the instability of the CpFe(cyclophane) radicals. The crystal structures of *anti*-[2₂](1,3)cyclophane, *anti*-4,12-dimethyl[2₂](1,3)cyclophane, and [2₅](1,2,3,4,5)cyclophane have been determined and show the benzene decks to be concave.²⁶⁻²⁸ Also, crystal structure determinations of iron complex 3 and a ruthenium complex of an *anti*-4,12-dimethyl[2₂](1,3)cyclophane show the benzene decks bound to the metal to be concave.^{29,30} On the other hand, the crystal structure of 1 shows the benzene deck bound to the metal to be convex.³¹ However, the stability of the neutral radical CpFe complexes in this series apparently is not strongly influenced by whether the deck bound to iron is concave or convex. Thus, exposure of the metal atom to solvent attack is not seen as a main factor contributing to the instability of these radicals.

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The transannular effect of the second benzene ring is also not a likely explanation. Measuring λ_{\max} of the charge-transfer bands of complexes of $[2_2](1,4)$ cyclophane and tetracyanoethylene (TCNE), Singer and Cram²⁶ concluded that $[2_2](1,4)$ cyclophane has a greater π basicity than *p*-xylene. Moinet et al.⁷ pointed out that increased π basicity of the arene (by methyl substitution) stabilized the CpFe(benzene) radical toward loss of arene. So the increased π basicity of the cyclophanes, if it were the only effect, should increase the stability of the radical.

Furthermore, changes in steric hindrance and π basicity would be expected to be quite small with respect to small changes in cyclophane structure. The large effects of structure on radical stability indicate a more important factor. These data suggest rather that the distortion of the coordinated benzene deck greatly affects the overlap of the metal and ligand orbitals and so controls the strength of the metal-arene bond. A similar explanation has been advanced by Elzinga and Rosenblum to explain the instability of $([2_2](1,4)\text{cyclophane})_2\text{Fe}^{2+}$ relative to $(\text{hexamethylbenzene})_2\text{Fe}^{2+}$.³³

Although the complete irreversibility of the $4^+/0$ couple may be evidence against this explanation, since the benzene decks of $[2_6](1,2,3,4,5,6)$ cyclophane are completely planar,²⁸ a different pathway may be available to this radical. Unfortunately the quantity of 4 available did not permit isolation and identification of its electrolysis products.

Finke et al. found that the geometry of the cyclophane was very important in determining the stability of the neutral product resulting from two electron reductions of $(\eta^6\text{-}[2_n]\text{cyclophane})\text{Ru}^{2+}$ complexes.¹⁶ Although the kinetic effects for their series of Ru(0) complexes were not as severe as in the present iron series, dependence was qualitatively similar with respect to the nature of the $[2_n]$ cyclophane ligand: the $[2_4](1,2,4,5)$ cyclophane complex was the most stable and the $[2_6](1,2,3,4,5,6)$ cyclophane complex was the least stable. However, the important $\eta^6\text{-}\eta^4$ isomerization of the arene-metal bond observed during reduction of the ruthenium complexes is either absent, or of much smaller consequence, for the iron series since the crystal structure of $\text{C}_5\text{Me}_5\text{FeC}_6\text{Me}_6$ has two planar rings.⁸

The high stability of the reduced complexes of $[2_4](1,2,4,5)$ cyclophane is the most striking similarity between the ruthenium and iron complexes. Apparently, the π system of this ligand is arranged to allow an efficient metal-ligand orbital overlap for both Fe(I) and Ru(0) perhaps similar to the stability enjoyed by complexes of the "chelating" diolefin cyclooctadiene.

A final interesting note is the reported photochemical lability of the Fe-arene bonds in these complexes. Parallels can be made between photochemistry and electrochemistry because both correspond to an occupation of the LUMO. Nesmeyanov³⁴ described the photodisproportionation of $[\text{CpFe}(\text{arene})]^+$ to ferrocene and free arene, implying a mechanism for the formation of these products similar to that involved in their electrochemical reduction. In view of this, it is quite surprising that Gill and Mann³⁵ report that *p*-xylene is more photolabile than $[2_2](1,4)$ -cyclophane when complexes to CpFe^+ . They attribute the greater stability of the cyclophane complex to the greater π basicity of the arene. This finding for the photoexcited cations is in contrast to our findings that the cyclophane

is less strongly complexed to a neutral CpFe fragment than are methyl-substituted benzenes.

Potential Trends of the $[\text{CpFe}(\text{cyclophane})]^+$ Reductions. The reductions of the CpFe(cyclophane) complexes are almost reversible chemically and thermodynamically, and cyclic voltammetry peak potentials are constant over a moderate range of scan rates (0.01–0.5 V/s). Thus, we feel that a discussion of relative E_p values in place of E° values is valid. The E_p of a reversible reduction will occur $28.5/n$ mV negative of the E° .³⁶

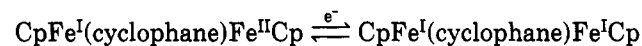
The potentials of the first reduction of the complexes are clearly dependent upon cyclophane structure. Although increasing the number of bridges may be modeled as increasing the number of alkyl substituents, the effect is not so simple. Furthermore, the methyl-substituted *anti*- $[2_2](1,3)$ cyclophane complexes 6, 9, and 10 reduced more easily than those of the unsubstituted *anti*- $[2_2](1,3)$ cyclophane complexes 5 and 8 (see Table I). This is in direct contrast to the usual effect of methyl substitution, which normally makes complexes more difficult to reduce.³ The ordering for ease of reduction (by peak potential) of the monoiron compounds is $2 \approx 3 > 1 \approx 4 \approx 6 > 5$.

Because the electron-donating nature of the alkyl groups does not seem to determine the reduction potentials, the reduction potential must be dependent upon the structure of the cyclophane. There are two possibilities: (1) the cyclophane structure controls the extent of metal-ligand interaction, thus determining the energy of the LUMO (which presumably has significant arene character⁸) or (2) the energy of the LUMO is dependent on the energy of the orbitals of the cyclophane that in turn are dependent on structure. Probably both effects are important.

The effect of cyclophane structure on redox potentials of $[(\text{C}_6\text{Me}_6)\text{Ru}(\text{cyclophane})]^{2+}/0$ and $[(\text{C}_5\text{H}_5)\text{Fe}(\text{cyclophane})]^{+}/0$ are quite comparable. The ordering for the ease of reduction of the ruthenium complexes is $[2_4](1,2,4,5)$ -cyclophane $> [2_2](1,4)$ cyclophane $> [2_5](1,2,3,4,5)$ -cyclophane $> \textit{anti}$ - $[2_2](1,3)$ cyclophane $> [2_5](1,2,3,4,5)$ -cyclophane $> [2_6](1,2,3,4,5,6)$ cyclophane $> \text{HMB}$. This parallel suggests that the energy of the LUMO relative to the HOMO of the complex depends largely on the energy of the orbitals of the cyclophane.

As in the comparison of chemical stabilities, the most similar result of the potential trends of the iron and ruthenium series is the ease of reduction of the complexes of $[2_4](1,2,4,5)$ cyclophane. The combination of the ease of reduction and chemical stability of the corresponding radical may be a result of the favorable orientation of the π orbitals in the arene ring.

For the bis(iron) complexes 7–10 the first reduction is 150–200 mV positive of the reduction of the corresponding mono(iron) complex, indicating that the CpFe^{II} fragment is electron withdrawing. The second reduction occurs, in all cases studied, within 30 mV of the reduction potential of the single iron complex (i.e., the potentials of steps B and D in Scheme II are approximately the same). Because the second reduction is



the CpFe^{I} fragment evidently has little effect on the energy level of the unreduced iron. As previously discussed (vide supra), the amount of separation between the first and second reduction potentials is dependent upon the amount of interaction between the irons.

Because the π - π transannular interaction has been demonstrated by other investigators³⁷ to be greater in free

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$[2_2](1,4)$ cyclophane than in *anti*- $[2_2](1,3)$ cyclophane, it is surprising that the two reductions of 7 and 8 show comparable potential separations (140 and 160 mV, respectively, Table Ib). Barring large structural rearrangements on complexation (an assumption supported by NMR evidence)^{12,13} with a resulting change in π - π interaction, the potential separation data indicate that the total Fe-Fe interaction is not composed solely of transannular interaction. Clearly, Fe-Ligand interaction contributes as well. Therefore if *anti*- $[2_2](1,3)$ cyclophane complexes, with less transannular interaction, have a total interaction comparable to $[2_2](1,4)$ cyclophane complexes, it must be due to a greater iron-ligand interaction in the *anti*- $[2_2](1,3)$ -cyclophane complexes. This is consistent with the structure of the cyclophanes: *anti*- $[2_2](1,3)$ cyclophanes, with a concave coordination site, are expected to have better overlap with metal orbitals than the $[2_2](1,4)$ cyclophane with a convex coordination site.

If, as Langer and Lehner³⁸ concluded, there is no transannular interaction between the arene rings of *anti*- $[2_2](1,3)$ cyclophane, one would expect a two-electron reduction for 8 corresponding to simultaneous reduction of both irons. The two one-electron reductions clearly indicate significant π - π transannular interaction in *anti*- $[2_2](1,3)$ cyclophanes, but this interaction cannot be quantitatively compared to that of other cyclophanes by measurement of potential separation without quantitative knowledge of the Fe-ligand interaction, solvation effects, and ion-pairing effects.

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Conclusions

(1) CpFe(cyclophane) radicals are not as stable as other CpFe(arene) radicals, probably because the distortion of the arene ring affects the overlap of metal and orbital ligands.

(2) The redox potential dependence on cyclophane structure in the CpFe⁺ series parallels the trend seen for HMB Ru²⁺ complexes. This suggests that redox potentials of the complexes depend upon the energy level of the π system in the ligand as well as on the extent of overlap of the metal and cyclophane orbitals.

(3) The complex of $[2_4](1,2,4,5)$ cyclophane is the easiest to reduce and the most stable after reduction. The color and *g* values observed in the ESR spectrum of the radical suggest differences in the higher energy molecular orbitals, compared to other CpFe(arene) complexes.

(4) The degree of Fe-Fe interaction in [(CpFe)₂(cyclophane)]²⁺ complexes, as measured by redox potential separation, depends on Fe-cyclophane interaction as well as π - π transannular interaction within the cyclophane. The total Fe-Fe interaction is comparable for all bis(iron) complexes studied.

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A Molecular Orbital Study of Bonding and Reactivity in Fe₄C Butterfly Clusters

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We report the results of molecular orbital calculations for the Fe₄C butterfly clusters $[\text{Fe}_4\text{C}(\text{CO})_{12}]^{2-}$, $[\text{HFe}_4\text{C}(\text{CO})_{12}]^-$, $\text{Fe}_4\text{C}(\text{CO})_{13}$, and $[\text{Fe}_4(\text{CO})_{12}(\text{C}-\text{CO}_2\text{CH}_3)]^-$. The structure of the clusters having an exposed carbon atom allows strong interactions between the carbido carbon and all four iron atoms in the cluster. In these clusters the molecular orbitals containing significant carbon character are stabilized, and the frontier orbitals are metal in character. The regioselectivity of the reactions interconverting $[\text{Fe}_4\text{C}(\text{CO})_{12}]^{2-}$, $[\text{HFe}_4\text{C}(\text{CO})_{12}]^-$, $\text{HFe}_4\text{CH}(\text{CO})_{12}$, and $\text{Fe}_4\text{C}(\text{CO})_{13}$ can be understood in terms of these metal frontier orbitals. The opening up of the iron butterfly that occurs when $\text{Fe}_4\text{C}(\text{CO})_{13}$ reacts with methanol to form $[\text{Fe}_4(\text{CO})_{12}(\text{C}-\text{CO}_2\text{CH}_3)]^-$ weakens the interaction between the carbido carbon p orbitals and the wingtip iron atoms. This change in geometry, which makes the carbon p orbitals more accessible for bonding to a substituent, appears to be necessary for reaction to occur at the carbido carbon atom.

Introduction

One of the more intriguing recent results in cluster chemistry is the observation that the single carbon atom in carbido carbonyl clusters can be transformed from an inert structural unit in high nuclearity clusters ($M_n\text{C}$, $n \geq 5$) to a center of chemical reactivity when these larger clusters are partially fragmented to give $M_4\text{C}$ clusters.^{1,2}

This phenomenon was first observed serendipitously in the reaction between $[\text{Fe}_6\text{C}(\text{CO})_{16}]^{2-}$ and tropylium bromide in methanol giving the μ_4 -methylidyne cluster $[\text{Fe}_4(\text{CO})_{12}(\text{C}-\text{CO}_2\text{CH}_3)]^-$ (eq 1).³ Subsequent work in several laboratories has resulted in the establishment of a family of Fe₄C clusters.⁴⁻⁶ The reactivity of the μ_4 -carbon atom

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