

Electrochemical Properties of $(\eta^6\text{-arene})\text{M}^{\text{II}}(\eta^5\text{-Et}_2\text{C}_2\text{B}_4\text{H}_4)$ Complexes: Formation of Persistent d^5 ($\text{M} = \text{Fe}, \text{Ru}$) and d^7 ($\text{M} = \text{Fe}$) Redox Products

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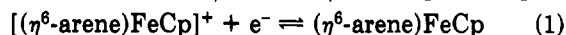
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Electrochemical oxidations and reductions of a series of mixed-carborane sandwich complexes $(\eta^6\text{-arene})\text{M}(\eta^5\text{-Et}_2\text{C}_2\text{B}_4\text{H}_4)$ ($\text{M} = \text{Fe}, \text{Ru}$) have been studied. Reversible one-electron oxidations are found. The Fe(III) cations were characterized by electron spin resonance spectroscopy at 77 K. Their spectra have axial symmetry with $g_{\parallel} > g_{\perp}$, consistent with a d^5 electronic configuration and a ground state analogous to the 2E_g state of the ferrocenium ion. Reductions of the Fe complexes gave persistent Fe(I) monoanions with orthorhombic g tensors very similar to those previously observed for isolectronic and isostructural $(\text{arene})\text{FeCp}$ ($\text{Cp} = \pi\text{-cyclopentadienyl}$) complexes. The d^7 complexes are assigned a ground state deriving from that of the ${}^2E_{1g}$ state of its higher symmetry analogues. The effect of substitution of Me for H on the arene ring gives a constant negative shift in E° throughout the series, the amount varying from -41 to -55 mV/Me, depending on solvent and oxidation state. The difference in E° values between the Fe(III)/Fe(II) and Fe(II)/Fe(I) couples is 3.10 ± 0.01 V. Oxidation of the Ru complexes in which arene = benzene or *p*-isopropyltoluene gave Ru(III) products that are stable for a few seconds at ambient temperatures.

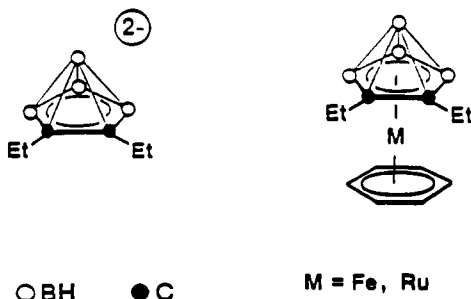
Introduction

The redox reactions of iron arene complexes are of significant interest.^{1,2} Virtually all of the previous studies have involved the Fe(II)/Fe(I) (d^6/d^7) couple of eq 1,²



where $\text{Cp} = (\eta^5\text{-C}_5\text{H}_5)$, the series of papers by Astruc and co-workers being particularly informative.^{1,3} Oxidation of these cationic Fe(II) arene complexes would provide an interesting comparison with the widely studied ferrocenium/ferrocene couple,⁴ but reported attempts at doing so have been thwarted by lack of reaction or by rapid decomposition of the Fe(III) dication.⁵ One older exception involved the use of SbCl_5 as oxidant: ESR spectra of oxidation products were diagnostic of Fe(III), but no further characterization was reported.⁶ An alternate approach to this problem is the substitution of Cp^- by ligand(s) that are more strongly electron-donating and/or have a more negative formal charge, thereby stabilizing the Fe(III) oxidation state.

The *nido*-carborane dianion $\text{R}_2\text{C}_2\text{B}_4\text{H}_4^{2-}$ (1) is isolectronic with the cyclopentadienyl anion and forms pentahapto complexes analogous to those involving Cp^- .⁷ In an earlier paper it was shown that substitution of $\text{C}_2\text{B}_4\text{H}_6^{2-}$ for C_5H_5^- resulted in an average stabilization of the M(III) oxidation state by over 600 mV in a series of Co and Fe sandwich complexes not involving arene ligands.⁸ Seen in this light, the recently prepared complexes of formula $(\eta^6\text{-arene})\text{Fe}(\text{Et}_2\text{C}_2\text{B}_4\text{H}_4)$ ⁹ appeared to be convenient precursors to Fe(III) arene sandwich complexes.



The electrochemical oxidation of a series of these Fe(II) complexes differing in the number of arene methyl groups was undertaken. One-electron oxidations were observed in which the Fe(III) products were sufficiently stable to be characterized by means of electrochemistry and ESR spectroscopy. A preliminary account of these results has appeared.^{10a} The potential of the reversible oxidation of $(\text{C}_6\text{Me}_6)\text{Fe}(\text{Et}_2\text{C}_2\text{B}_4\text{H}_4)$ ($E^\circ = +0.19$ V versus Fc) is over 1 V negative of the (irreversible) oxidation of $(\text{C}_6\text{Me}_6)\text{-FeCp}^+$.^{10b}

The ferracarborane complexes may also be reduced by one electron in THF to reasonably persistent anions with E° values in the range of -2.6 to 2.9 V versus Fc. For the compounds $(\text{C}_6\text{Me}_x\text{H}_{6-x})\text{Fe}(\text{Et}_2\text{C}_2\text{B}_4\text{H}_4)$, $x = 0-6$, the difference between E° values of the Fe(III)/Fe(II) and Fe(II)/Fe(I) couples is constant ($3.10 + 0.01$ V). The elec-

(1) (a) Astruc, D. *Acc. Chem. Res.* 1986, 19, 377. (b) Astruc, D. In *The Chemistry of the Metal-Carbon Bond*; Hartley, F. R., Patai, S., Eds.; Wiley: New York, 1987; Vol. 4, p 625. (c) Astruc, D. *Comments Inorg. Chem.* 1987, 6, 61. (d) Astruc, D. *Chem. Rev.* 1988, 88, 1189.

(2) Sutherland, R. G.; Iqbal, M.; Piorko, A. *J. Organomet. Chem.* 1986, 302, 307.

(3) See: Desbois, M.-H.; Astruc, D.; Guillin, J.; Varret, F.; Trautwein, A. X.; Villeneuve, G. *J. Am. Chem. Soc.* 1989, 111, 5800 and previous papers in the series. For reductions of Fe(II) cyclophane complexes, see: Bowyer, W. J.; Geiger, W. E.; Boekelheide, V. *Organometallics* 1984, 3, 1079.

(4) Certain aspects of the ferrocenium/ferrocene couple have been recently reviewed; see: Geiger, W. E. In *Organometallic Radical Processes*; Trogler, W. C., Ed.; Elsevier: Amsterdam, 1990; Chapter 5, especially pp 146-152.

(5) (a) Nesmeyanov, A. N.; Vol'kenau, N. A.; Sirotkina, E. I.; Deryabin, V. V. *Dokl. Akad. Nauk SSSR* 1967, 177, 1170 (Eng)/1110 (Russ). (b) Nesmeyanov, A. N.; Vol'kenau, N. A.; Sirotkina, E. I. *Izv. Akad. Nauk SSSR, Ser. Khim.* 1967, 1142 (Eng)/1170 (Russ). (c) Morrison, W. H., Jr.; Ho, E. Y.; Hendrickson, D. N. *J. Am. Chem. Soc.* 1974, 96, 3603. (d) Astruc, D. *Tetrahedron* 1983, 39, 4027.

(6) Solodovnikov, S. P.; Nesmeyanov, A. N.; Vol'kenau, N. A.; Kotova, L. S. *J. Organomet. Chem.* 1980, 201, C45.

(7) Grimes, R. N. In *Advances in Boron and the Boranes*; Liebman, J. F., Greenberg, A., Williams, R. E., Eds.; VCH Publishers: New York, 1988; Chapter 11, pp 235-263 and references therein.

(8) Geiger, W. E.; Brennan, D. E. *Inorg. Chem.* 1982, 21, 1963. (9) (a) Swisher, R. G.; Sinn, E.; Grimes, R. N. *Organometallics* 1983, 2, 506. (b) Micciche, R. P.; Sneddon, L. G. *Organometallics* 1983, 2, 674 (toluene complex).

(10) (a) Merkert, J. W.; Geiger, W. E.; Davis, J. H., Jr.; Attwood, M. D.; Grimes, R. N. *Organometallics* 1989, 8, 1580. (b) Merkert, J. W. Ph.D. Thesis, University of Vermont, 1991.

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Table I. Cyclic Voltammetry Data for M(III)/M(II) Couples for Complexes Studied in CH₂Cl₂/0.1 M Bu₄NPF₆ (Potentials versus Cp₂Fe^{0/+})

compound	E ^o , V	X vs Fc ^a	ΔE _p ^b , mV	i _c /i _a ^c
(C ₆ Me ₆)Fe(Et ₂ C ₂ B ₄ H ₄)	+0.190	0.75	63	0.95
(C ₆ Me ₅ H)Fe(Et ₂ C ₂ B ₄ H ₄)	+0.251	0.74	72	0.94
(C ₆ Me ₄ H ₂)Fe(Et ₂ C ₂ B ₄ H ₄) ^d	+0.294	0.61	79	0.96
(1,3,5-C ₆ Me ₃ H ₃)Fe-(Et ₂ C ₂ B ₄ H ₄)	+0.373	0.70	69	0.92
(1,4-C ₆ Me ₂ H ₄)Fe-(Et ₂ C ₂ B ₄ H ₄)	+0.421		70	0.97
(C ₆ MeH ₅)Fe(Et ₂ C ₂ B ₄ H ₄)	+0.467	0.74	69	0.86
(C ₆ H ₅)Fe(Et ₂ C ₂ B ₄ H ₄)	+0.517		77	0.95
(C ₆ H ₅)Fe(Bu ₂ C ₂ B ₄ H ₄)	+0.54		86	0.94
[(C ₆ Me ₆)FeCp] ⁺	+1.28		irrev	
(cymene)Ru(Et ₂ C ₂ B ₄ H ₄) ^e	+0.75	0.70	85	0.70
(C ₆ H ₅)Ru(Et ₂ C ₂ B ₄ H ₄)	+0.85	0.70	84	0.54

^a Current function, $i_p/Cv^{1/2}$, of the complex divided by that of Fc. ^b $E_{pa} - E_{pc}$ with $v = 0.10$ V/s. ^c Value with $v = 0.10$ V/s, calculated by the method of: Nicholson *Anal. Chem.* 1965, 37, 1351. ^d 1,2,4,5-Isomer. ^e Cymene = *p*-isopropyltoluene.

trochemical and ESR properties of the Fe(I) products are similar to the (arene)FeCp complexes studied in detail by Astruc and co-workers.^{1,3}

Analogous investigations of a more limited scope were pursued for (arene)Ru(Et₂C₂B₄H₄) complexes. Related cyclopentadienyl complexes, [(arene)RuCp]⁺, undergo irreversible oxidations.¹¹ In contrast, the one-electron oxidations of (arene)Ru(Et₂C₂B₄H₄) are reversible at moderate cyclic voltammetric (CV) sweep rates, allowing measurement of the E^o value of the Ru(III)/Ru(II) couple.

A brief report has recently appeared describing the reversible oxidation and reduction of (C₆Me₆)Fe(η⁴-Bu₂C₂P₂).¹² This complex possesses a formally dinegative heterocyclobutadienyl ligand analogous to (Et₂C₂B₄H₄)²⁻.

Experimental Section

Electrochemistry. Electrochemical procedures have been previously detailed.¹³ The reference electrode used in experiments was either the SCE or an Ag/AgCl electrode. Potentials in this paper are referenced, however, to the Cp₂Fe^{+/0} couple, according to IUPAC recommendations.¹⁴ Ferrocene was added as an internal standard to the analyte solutions. Addition of +0.46 V (CH₂Cl₂) or +0.56 V (THF) converts these potentials back to SCE values for comparison with earlier literature. The supporting electrolyte was 0.1 M Bu₄NPF₆ in all cases. The working electrode was Pt, but data on reductions in THF were also recorded at a mercury electrode without change in redox behavior. Concentrations of analytes were 0.4–0.6 mM for both CV experiments and bulk electrolyses. A luggin probe was employed in CV experiments to minimize errors from uncompensated resistance.¹⁵ The reported values of E^o were obtained by averaging the cathodic and anodic peak potentials for a redox couple at several different scan rates in a replicate fashion. The relative standard deviations of these values were approximately 5 mV.

Electron Spin Resonance Measurements. All spectra were recorded at 77 K on a modified Varian E-3 spectrometer equipped with a frequency meter and using DPPH as a field calibrant.

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(12) Driess, M.; Hu, D.; Pritzkow, H.; Schaeufele, H.; Zenneck, U.; Regitz, M.; Roesch, W. *J. Organomet. Chem.* 1987, 334, C35.

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(14) Gritzner, G.; Kuta, J. *Pure Appl. Chem.* 1984, 56, 461.

(15) Sawyer, D. T.; Roberts, J. L. *Experimental Electrochemistry for Chemists*; Wiley-Interscience Publishers: New York, 1974; p 347.

Table II. Cyclic Voltammetry Data for M(III)/M(II) Couples for Complexes Studied in THF/0.1 M Bu₄NPF₆ (Potentials versus Cp₂Fe^{0/+})

compound	E ^o , V	X vs Fc ^a	ΔE _p ^b , mV	i _c /i _a ^c
(C ₆ Me ₆)Fe(Et ₂ C ₂ B ₄ H ₄)	+0.237		119 ^d	1.00
(C ₆ Me ₅ H)Fe(Et ₂ C ₂ B ₄ H ₄)	+0.279	0.76	78	0.95
(C ₆ Me ₄ H ₂)Fe(Et ₂ C ₂ B ₄ H ₄) ^e	+0.312	0.78	75	0.80
(1,3,5-C ₆ Me ₃ H ₃)Fe-(Et ₂ C ₂ B ₄ H ₄)	+0.369		79	0.84
(1,4-C ₆ Me ₂ H ₄)Fe-(Et ₂ C ₂ B ₄ H ₄)	+0.413	1.0	83	0.81
(C ₆ MeH ₅)Fe(Et ₂ C ₂ B ₄ H ₄)	+0.464	0.77	94	0.83
(C ₆ H ₅)Fe(Et ₂ C ₂ B ₄ H ₄)	+0.505	0.78	113	irrev ^f

^a Current function, $i_p/Cv^{1/2}$, of the complex divided by that of Fc. ^b $E_{pa} - E_{pc}$ with $v = 0.10$ V/s. ^c Value with $v = 0.10$ V/s, calculated by the method of Nicholson. ^d $T = 273$ K in experiment without luggin probe. ^e 1,2,4,5-Isomer. ^f $i_c/i_a = 0.65$ with $v = 0.20$ V/s.

Table III. Cyclic Voltammetry Data for M(II)/M(I) Couples for Complexes Studied in THF/0.1 M Bu₄NPF₆ (Potentials versus Cp₂Fe^{0/+})

compound	E ^o , V	X vs Fc ^a	ΔE _p ^b , mV	i _c /i _a ^c
(C ₆ Me ₆)Fe(Et ₂ C ₂ B ₄ H ₄)	-2.846		96	0.90
(C ₆ Me ₅ H)Fe(Et ₂ C ₂ B ₄ H ₄)	-2.809	0.84	89	0.92 ^d
(C ₆ Me ₄ H ₂)Fe(Et ₂ C ₂ B ₄ H ₄) ^f	-2.774	0.76	84	0.94 ^e
(1,3,5-C ₆ Me ₃ H ₃)Fe-(Et ₂ C ₂ B ₄ H ₄)	-2.729		78	0.88
(1,4-C ₆ Me ₂ H ₄)Fe-(Et ₂ C ₂ B ₄ H ₄)	-2.696	1.0	89	0.93
(C ₆ MeH ₅)Fe(Et ₂ C ₂ B ₄ H ₄)	-2.654	0.81	96 ^d	0.86
(C ₆ H ₅)Fe(Et ₂ C ₂ B ₄ H ₄)	-2.595	0.77	68	0.87
(C ₆ Me ₆)FeCp ⁺	ca. -2.37 ^g			

^a Current function, $i_p/Cv^{1/2}$, of the complex divided by that of Fc. ^b $E_{pa} - E_{pc}$ with $v = 0.10$ V/s. ^c Value with $v = 0.10$ V/s, calculated by the method of Nicholson. ^d Scan rate = 0.20 V/s. ^e Scan rate = 0.05 V/s. ^f 1,2,4,5-Isomer. ^g Hamon, J.-R.; Astruc, D.; Michaud, P. *J. Am. Chem. Soc.* 1981, 103, 758.

Solutions of Fe(III) complexes were produced through bulk anodic oxidation of the corresponding Fe(II) complexes. Solutions of Fe(I) complexes were prepared by reduction of a few milligrams of the Fe(II) complexes over a freshly distilled sodium mirror under high vacuum. The Fe(II) solution was left in contact with the mirror for sufficient time to allow a color change (usually 30 s at ca. 200 K) and then quenched in liquid nitrogen. In some cases, this reaction period was insufficient for detectable conversion to the monoanion, so the thawed sample was reexposed to the Na mirror at 200 K for another 30 s. This procedure was repeated until a spectrum was observed.

Compounds. The (arene)Fe(Et₂C₂B₄H₄) complexes were prepared by thermal displacement of cyclooctatriene from (η⁶-C₈H₁₀)Fe(Et₂C₂B₄H₄) as described elsewhere.^{9a,16} The synthesis and characterization of the cymene- and benzene-ruthenium complexes were reported earlier.¹⁷

Results and Discussion

Iron Complexes. Voltammetric Behavior and Preparation of Redox Products. Each of the η⁶-arene-Fe(II) compounds¹⁸ undergoes one oxidation and one

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(17) Davis, J. H., Jr.; Sinn, E.; Grimes, R. N. *J. Am. Chem. Soc.* 1989, 111, 4776.

(18) All of the arene complexes in this paper are assumed to be hexahaptoordinated in all oxidation states. Eighteen-electron arene carborane complexes have been shown to have planar arenes; see refs 9a and 17; also: Swisher, R. G.; Butcher, R. J.; Sinn, E.; Grimes, R. N. *Organometallics* 1985, 4, 882. Swisher, R. G.; Sinn, E.; Grimes, R. N. *Organometallics* 1985, 4, 890. Micciche, R. P.; Sneddon, L. G. *Organometallics* 1983, 2, 674. Coordination in the η⁶ mode has been demonstrated for (η-arene)Fe complexes containing 19 or 20 valence electrons (for leading references, see: Astruc, D.; Mandon, D.; Madonik, A.; Michaud, P.; Ardoin, N.; Varret, F. *Organometallics* 1990, 9, 2155).

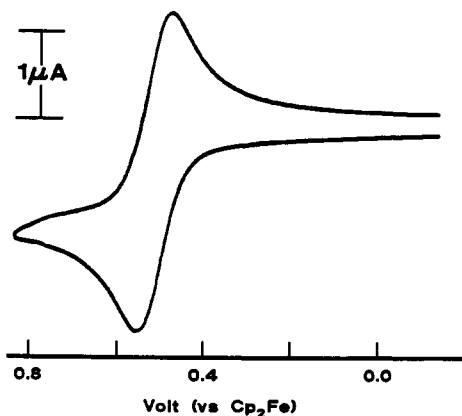
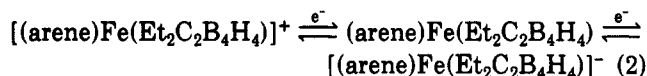


Figure 1. CV scan of 0.56 mM $(\text{C}_6\text{Me}_6)\text{Fe}(\text{Et}_2\text{C}_2\text{B}_4\text{H}_4)$ in $\text{CH}_2\text{Cl}_2/0.1 \text{ M Bu}_4\text{NPF}_6$ at ambient temperature, $\nu = 0.20 \text{ V/s}$, Pt electrode.

reduction process, resulting in corresponding Fe(III) and Fe(I) complexes, respectively (eq 2).



transfer reactions are detectable in THF, owing to the relatively large potential window of this solvent. The oxidations alone were detectable in CH_2Cl_2 . However, the Fe(III) electrode products were generally more stable in the latter solvent, so bulk electrolytic oxidations employed CH_2Cl_2 .

Tables I–III summarize the most important cyclic voltammetry data on the iron complexes. Each couple was diffusion-controlled, as evidenced by a constant current function ($i_p/C\nu^{1/2}$) over at least 1 order of magnitude change in scan rate (usually 0.05–0.50 V/s). Values of ΔE_p were in the range expected for fast one-electron couples in resistive solvents (Tables I–III) and were always close to those observed for the $\text{Cp}_2\text{Fe}^{0/+}$ couple in the same solution. Current functions of the couples were essentially the same within the set of carborane complexes, implying that the number of electrons transferred was the same in all reactions (one electron by coulometry). Ratios of current functions for the carborane complexes to that of ferrocene were about 0.7–0.9 (Tables I–III), which may be interpreted in terms of slightly lower diffusion coefficients for the arene complexes as compared to ferrocene. Coulometric experiments on selected compounds (vide infra) also established that these redox couples are one-electron reactions.

The i_c/i_a values in Table II indicate that the Fe(III) monocations, $(\text{arene})\text{Fe}(\text{Et}_2\text{C}_2\text{B}_4\text{H}_4)^+$, exhibit decreasing kinetic stabilities when the arene is less fully substituted, at least in THF. Thus, with a scan rate of 0.1 V/s, the hexamethylbenzene complex displays full chemical reversibility, whereas the benzene complex has an essentially irreversible oxidation. This behavior is reminiscent in a qualitative sense of trends observed in the redox properties of rhodium arene complexes.¹³ There is no detectable trend in stabilities for the cations in dichloromethane, since half-lives of the Fe(III) complexes are all in excess of the CV time scale. Chemical reversibility of the reductions in THF is also high, and no clear trend toward lower lifetimes of less highly substituted arene complexes was noted from the CV data. Typical CV scans are shown in Figures 1 and 2.

The voltammetry data suggested that the Fe(III) and Fe(I) complexes might be generated in situ and characterized by spectroscopic methods, and this proved to be

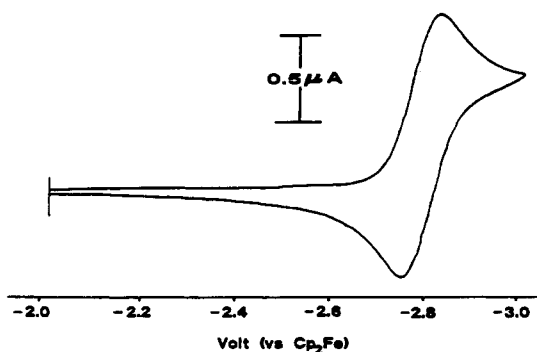


Figure 2. CV scan of 0.76 mM $(\text{C}_6\text{Me}_6)\text{Fe}(\text{Et}_2\text{C}_2\text{B}_4\text{H}_4)$ in $\text{THF}/0.1 \text{ M Bu}_4\text{NPF}_6$, $T = 297 \text{ K}$, $\nu = 0.05 \text{ V/s}$, hanging Hg drop electrode.

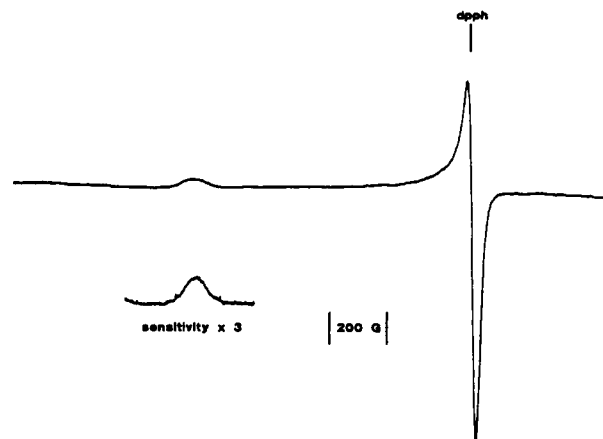


Figure 3. ESR spectrum of the Fe(III) monocation, $[(\text{C}_6\text{Me}_6)\text{Fe}(\text{Et}_2\text{C}_2\text{B}_4\text{H}_4)]^+$, generated by coulometric oxidation of the Fe(II) precursor. Spectral conditions: solvent, CH_2Cl_2 ; $T = 77 \text{ K}$. The parallel g -tensor resonance is shown at higher recorder sensitivity in the insert.

Table IV. Electron Spin Resonance Results for Paramagnetic Complexes Generated in These Studies^a

complex	method	ox. state	g values
$(\text{C}_6\text{Me}_6)\text{Fe}(\text{Et}_2\text{C}_2\text{B}_4\text{H}_4)^+$	anodic ox. ^b	Fe(III)	$g_{\parallel} = 2.486$, $g_{\perp} = 2.002$
$(\text{C}_6\text{Me}_6)\text{Fe}(\text{Et}_2\text{C}_2\text{B}_4\text{H}_4)^-$	Na ^c	Fe(I)	$g_1 = 2.062$, $g_2 = 1.999$, $g_3 = 1.909$
$(\text{C}_6\text{Me}_3\text{H}_3)\text{Fe}(\text{Et}_2\text{C}_2\text{B}_4\text{H}_4)^-$	Na ^c	Fe(I) ^d	$g_1 = 2.062$, $g_2 = 1.998$, $g_3 = 1.916$

^a All spectra recorded at 77 K. ^b Solvent was CH_2Cl_2 . ^c Solvent was THF. ^d Sample showed additional shoulders at $g = 2.030$ and 1.973.

so. The complex chosen for these experiments was $(\text{C}_6\text{Me}_6)\text{Fe}(\text{Et}_2\text{C}_2\text{B}_4\text{H}_4)$. Bulk electrolytic oxidation of this complex in CH_2Cl_2 ($T = 255 \text{ K}$) at $E_{\text{appl}} = +0.60 \text{ V}$ released 1.01 faraday and resulted in a green-brown solution displaying a strong ESR signal (Figure 3 and Table IV) with an axial g tensor, $g_{\parallel} = 2.486$ and $g_{\perp} = 2.002$. As discussed below, the g values are those expected for a d^5 , Fe(III) complex and are therefore assigned to $[(\text{C}_6\text{Me}_6)\text{Fe}(\text{Et}_2\text{C}_2\text{B}_4\text{H}_4)]^+$. Neither the Fe(III) cation nor the Fe(I) anions had detectable fluid solution ESR spectra.

Bulk reduction of the Fe(II) complex in THF at $T = 273 \text{ K}$ gave the anion $[(\text{C}_6\text{Me}_6)\text{Fe}(\text{Et}_2\text{C}_2\text{B}_4\text{H}_4)]^-$ in low yield, as shown by rotating Pt electrode voltammetry.¹⁹ The

(19) Rotating Pt electrode voltammetry after electrolysis revealed a plateau current essentially equal in value to that measured prior to electrolysis, but with only 10% of the current being anodic. Therefore 90% of the anion had reoxidized to the original reactant.

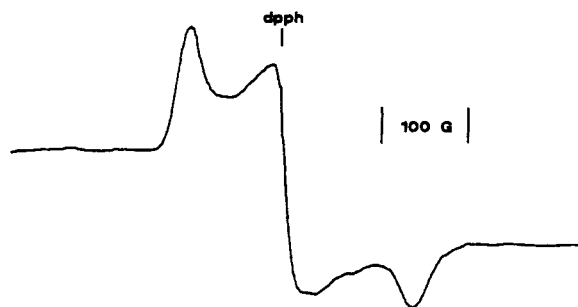


Figure 4. ESR spectrum of the Fe(I) monoanion, $[(C_6Me_6)Fe(Et_2C_2B_4H_4)]^-$, generated by reduction of the Fe(II) precursor with Na under vacuum. Spectral conditions: solvent, THF; $T = 77$ K.

anion was very prone toward oxidation to starting material under drybox conditions and transfer of the reduced solutions to ESR sample tubes was unsuccessful.

Consequently, the ESR spectra of anions in this series, $[(arene)Fe(Et_2C_2B_4H_4)]^-$, were generated by alkali metal reductions of the Fe(II) complexes under high-vacuum conditions. An approximately 2 mM solution of $(C_6Me_6)Fe(Et_2C_2B_4H_4)$ in THF was allowed brief contact with a freshly prepared sodium mirror at 200 K. After the solution turned brown it was quenched in liquid N_2 , yielding the ESR spectrum in Figure 4. An orthorhombic g tensor is evident, with the principal values given in Table IV. Close inspection of this spectrum reveals two other noteworthy features. One is a sharp signal at $g = 2.00$, barely evident in Figure 4. This feature became much more prominent when the sample was warmed to room temperature and then refrozen. It is assigned to a decomposition product, most likely an organic radical. The second is a pair of features appearing as shoulders on the middle g feature of Figure 4. Since changes in sample temperature had no apparent effect on the intensity of the shoulders, these extra features may be indigenous to the Fe(I) complexes rather than to decomposition products. A possible explanation for their presence is the possibility of two chemically inequivalent lattice sites for the radical. This phenomenon has been documented for metal sandwich radicals^{20,21} and as many as four inequivalent sites have been found for analogous $(arene)FeCp$ radicals.²¹ A strong site dependence of the host lattice is often an indication that the radical has an electronic ground state with one or more low-lying excited states. This is consistent with our description of the ground state of $[(arene)Fe(Et_2C_2B_4H_4)]^-$ as derived from the d_{xz} , d_{yz} pair, which is degenerate (as ${}^2E_{1g}$) in metal radicals of axial symmetry.

Ruthenium Complexes. Electrochemical Behavior.

Two complexes of the type $(arene)Ru(Et_2C_2B_4H_4)$ were investigated, the arene ligand being either benzene or *p*-cymene (*p*-isopropyltoluene). Table I gives the pertinent voltammetric data. The Ru(II)/Ru(III) couples are slightly over 300 mV more positive than those of the iron analogues. That the redox processes involve a one-electron change is evident from the anodic current functions, which are essentially equal to those of the Fe complexes, and the ΔE_p values, again typical of reversible one-electron couples in CH_2Cl_2 . No reductions of the Ru complexes were observed.

Unlike the Fe complexes in dichloromethane, the Ru(III) oxidation product was unstable. From i_c/i_a values as a function of scan rate it was concluded that the half-lives of the benzene and *p*-cymene complexes were 2.1 and 3.4 s, respectively, at room temperature. The current function of $(C_6H_6)Ru(Et_2C_2B_4H_4)$, which was constant when $v > 0.30$ V/s, rose significantly at lower scan rates, implying electroactive decomposition products. Bulk coulometric oxidation of the benzene complex at 230 K released 2.0 faraday as the solution went from orange to green. A series of irreversible product waves resulted and no products were identified. A sample taken midway through the electrolysis and frozen for ESR analysis did not give a signal.

Electronic Ground States of the Fe(III) and Fe(I) Complexes. The ESR results provide a basis for assignment of the electronic ground states for the Fe(III) complex $[(arene)Fe(Et_2C_2B_4H_4)]^+$ and the Fe(I) complex $[(arene)Fe(Et_2C_2B_4H_4)]^-$. The groundwork for this treatment is the detailed ESR literature on analogous iron sandwich complexes. The present carborane complexes possess a ligand field of, at best, C_s symmetry. However, analogous complexes have been successfully treated assuming a pseudoaxial symmetry, and we shall make reference in this discussion to those ground states derived from the higher symmetry notation.²¹

The d^5 ferrocenium ion, like many other sandwich complexes with degenerate or nearly degenerate ground states,²⁰ has g values that are quite dependent on matrix conditions. However, it is always true that $g_{\parallel} > g_{\perp}$.²² Isoelectronic mixed sandwich complexes containing a dicarbollide ligand were shown to have similar properties with $g_{\parallel} > g_{\perp}$.²³ For example, $g_{\parallel} = 3.579$, $g_{\perp} = 1.778$ for the Fe(III) complex $CpFe(B_9C_2H_{11})$. These data have been interpreted in terms of a ${}^2E_{2g}$ ground state for the Fe(III) complexes, with a SOMO²⁴ comprised almost entirely of the metal d_{xy} and $d_{x^2-y^2}$ orbitals.^{20,22} The other likely ground state for the Fe(III) system, ${}^2A_{1g}$, would display small g -value anisotropy and much longer relaxation rates, so that ESR spectra would be observed in fluid solutions. The prior available ESR data on Fe(III) arene complexes are similar.^{6,12}

The fact that the ESR spectrum of $[(C_6Me_6)Fe(Et_2C_2B_4H_4)]^+$ is observable only in frozen media and that $g_{\parallel} > g_{\perp}$ argues strongly for a ground state for the Fe(III) complex derived from ${}^2E_{2g}$, i.e., one involving a SOMO of either d_{xy} or $d_{x^2-y^2}$, with the unoccupied member of the pair lying just above the other in energy.

The orthorhombic g tensors of the Fe(I) complexes $[(arene)Fe(Et_2C_2B_4H_4)]^-$ are very similar to those observed for the analogous $(arene)FeCp$ complexes.²¹ Single-crystal studies allowed assignment of the principal directions of the g tensor, $g_y = 2.062$, $g_x = 2.002$, $g_z = 1.912$ for $(C_6Me_6)FeCp$,²¹ and the similarity of our g values (Table IV) to those of the cyclopentadienyl analogues suggests a similar interpretation. Since the ground state in the latter was assigned as ${}^2E_{1g}$, a similar assignment is offered here for the d^7 Fe(I) complexes, with the SOMO comprised mostly of either metal d_{xz} or d_{yz} , this pair being expected to be almost degenerate.

Dependence of E° Values on Arene Substituents.

A number of authors have commented on the dependence of the formal potentials of $(arene)M$ complexes on the number of methyl groups contained by the arene. We have recently summarized the available data and discussed it in the context of results on $(\eta\text{-arene})RhCp^{*2+}/0$.^{13,25} The

(20) See: Ammeter, J. H. *J. Magn. Reson.* 1978, 30, 299.

(21) Rajasekharan, M. V.; Giezynski, S.; Ammeter, J. H.; Oswald, N.; Michaud, P.; Hamon, J. R.; Astruc, D. *J. Am. Chem. Soc.* 1982, 104, 2400. A reviewer states that an explanation of the shoulders as arising from inequivalent lattice sites is less probable for frozen glasses than, say, from magnetically dilute powders.

(22) Prins, R. *Mol. Phys.* 1970, 19, 603.

(23) Maki, A. H.; Berry, T. E. *J. Am. Chem. Soc.* 1965, 87, 4437.

(24) SOMO stands for semiooccupied molecular orbital.

Table V. Slopes of Plots of E° versus the Number of Methyl Groups on Arene in Complexes $(\text{arene})\text{Fe}(\text{Et}_2\text{C}_2\text{B}_4\text{H}_4)$

couple	solvent	slope, mV	correl coeff
$(\text{arene})\text{Fe}(\text{Et}_2\text{C}_2\text{B}_4\text{H}_4)^{+/0}$	CH_2Cl_2	-55	0.996
$(\text{arene})\text{Fe}(\text{Et}_2\text{C}_2\text{B}_4\text{H}_4)^{+/0}$	THF	-45	0.999
$(\text{arene})\text{Fe}(\text{Et}_2\text{C}_2\text{B}_4\text{H}_4)^{0/-}$	THF	-41	0.996

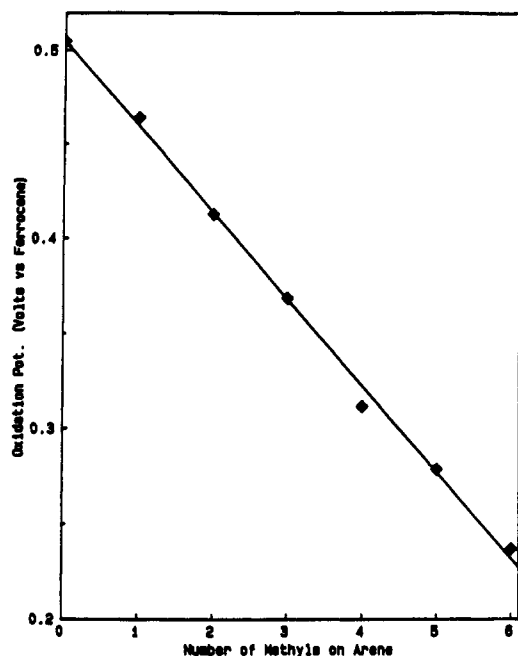


Figure 5. Plot of the E° of the Fe(III)/Fe(II) couple for the complexes $[(\text{C}_6\text{Me}_2\text{H}_{6-x})\text{Fe}(\text{Et}_2\text{C}_2\text{B}_4\text{H}_4)]^{+/0}$ measured in THF as a function of the number of Me groups, x , on the arene.

iron complexes that are the subject of the present paper provide the first opportunity to evaluate the methyl substituent effect for d^5/d^6 and d^6/d^7 couples based on the same complex. Excellent linear fits were obtained between the E° values of Tables I–III and the number of methyl groups on the arene. Table V gives the slopes and correlation coefficients for these plots, a sample of which is Figure 5. In each case the direction of the E° shift is as expected: negative with increasing methyl substitution. The amount of the shift for the Fe(III)/Fe(II) couple is slightly greater in CH_2Cl_2 (-55 mV/Me) than in THF (-45 mV/Me). The shift in THF is essentially equal for the Fe(III)/Fe(II) and Fe(II)/Fe(I) couples (the latter, -41 mV/Me).

The arene Me group effects on E° are somewhat larger than the average reported in the previous literature (-28 mV/Me¹³), which is subject to considerable scatter. All of the studies on Me substituent effects have involved couples in which the redox orbital is located largely or entirely on the metal. The negative shift of 30–55 mV/Me surely arises from the inductive effect of the Me group. The shift appears to be linearly additive as from one to

(25) Howell, J. O.; Goncalves, J. M.; Amatore, C.; Klasinc, L.; Wightman, R. M.; Kochi, J. K. *J. Am. Chem. Soc.* 1984, 106, 3968.

six Me groups are added to the arene ring, for both the d^5 – d^6 and d^6 – d^7 couples.

Conclusions

The present results indicate that the small carborane ligand $\text{Et}_2\text{C}_2\text{B}_4\text{H}_4^{2-}$ is capable of imparting significant stabilization, both thermodynamic and kinetic, to Fe(III) and Ru(III) complexes, compared to their cyclopentadienyl counterparts. Although the corresponding Fe(I) carborane complexes are thermodynamically destabilized (more negative reductions) compared to the Cp analogues, they are sufficiently persistent to be characterized by ESR spectroscopy. As far as the SOMO's are concerned, there is no evidence for significant alterations in electronic structures for d^5 or d^7 complexes when Cp is replaced by $\text{Et}_2\text{C}_2\text{B}_4\text{H}_4$.

Following many unsuccessful attempts to prepare persistent Fe(III) arene complexes,^{5,26} it now appears that reversible oxidations of Fe(II) arene complexes will be common for neutral complexes containing a strongly electron-donating ancillary ligand. In addition to the present data, two other voltammetric studies support this statement. The oxidation of $(\eta^6\text{-toluene})\text{Fe}(\eta^4\text{-}^i\text{Bu}_2\text{C}_2\text{P}_2)$ ($E^\circ = +0.55$ V versus SCE) yields the corresponding Fe(III) monocation with an axial g tensor, $g_{\parallel} = 2.53$, $g_{\perp} = 2.01$.¹² Similarly, oxidation of the zwitterionic complex $(\eta^5\text{-C}_5\text{Ph}_5)\text{Fe}[\eta^6\text{-C}_6\text{H}_5(\text{C}_5\text{Ph}_4)]$, which has a tetraphenylcyclopentadienyl anion as a substituent on the arene ring, is reversible, $E^\circ = -0.15$ V versus ferrocene.^{26,27}

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Registry No. THF, 109-99-9; $(\text{C}_6\text{Me}_6)\text{Fe}(\text{Et}_2\text{C}_2\text{B}_4\text{H}_4)$, 84583-01-7; $(\text{C}_6\text{Me}_5\text{H})\text{Fe}(\text{Et}_2\text{C}_2\text{B}_4\text{H}_4)$, 135480-72-7; $(\text{C}_6\text{Me}_4\text{H}_2)\text{Fe}(\text{Et}_2\text{C}_2\text{B}_4\text{H}_4)$, 135480-73-8; $(1,3,5\text{-C}_6\text{Me}_3\text{H}_3)\text{Fe}(\text{Et}_2\text{C}_2\text{B}_4\text{H}_4)$, 84583-00-6; $(1,4\text{-C}_6\text{Me}_2\text{H}_4)\text{Fe}(\text{Et}_2\text{C}_2\text{B}_4\text{H}_4)$, 135480-74-9; $(\text{C}_6\text{MeH}_5)\text{Fe}(\text{Et}_2\text{C}_2\text{B}_4\text{H}_4)$, 84583-02-8; $(\text{C}_6\text{H}_6)\text{Fe}(\text{Et}_2\text{C}_2\text{B}_4\text{H}_4)$, 84582-99-0; $(\text{C}_6\text{H}_6)\text{Fe}(\text{Bu}_2\text{C}_2\text{B}_4\text{H}_4)$, 129248-86-8; $[(\text{C}_6\text{Me}_6)\text{FeCp}]^+$, 54688-69-6; (cymene)Ru($\text{Et}_2\text{C}_2\text{B}_4\text{H}_4$), 121141-52-4; $(\text{C}_6\text{H}_6)\text{Ru}(\text{Et}_2\text{C}_2\text{B}_4\text{H}_4)$, 120771-69-9; $[(\text{C}_6\text{Me}_6)\text{Fe}(\text{Et}_2\text{C}_2\text{B}_4\text{H}_4)]^+$, 135480-75-0; $[(\text{C}_6\text{Me}_5\text{H})\text{Fe}(\text{Et}_2\text{C}_2\text{B}_4\text{H}_4)]^+$, 135480-76-1; $[(\text{C}_6\text{Me}_4\text{H}_2)\text{Fe}(\text{Et}_2\text{C}_2\text{B}_4\text{H}_4)]^+$, 135480-77-2; $[(1,3,5\text{-C}_6\text{Me}_3\text{H}_3)\text{Fe}(\text{Et}_2\text{C}_2\text{B}_4\text{H}_4)]^+$, 135480-78-3; $[(1,4\text{-C}_6\text{Me}_2\text{H}_4)\text{Fe}(\text{Et}_2\text{C}_2\text{B}_4\text{H}_4)]^+$, 135480-79-4; $[(\text{C}_6\text{MeH}_5)\text{Fe}(\text{Et}_2\text{C}_2\text{B}_4\text{H}_4)]^+$, 135480-80-7; $[(\text{C}_6\text{H}_6)\text{Fe}(\text{Et}_2\text{C}_2\text{B}_4\text{H}_4)]^+$, 120771-70-2; $[(\text{C}_6\text{H}_6)\text{Fe}(\text{Bu}_2\text{C}_2\text{B}_4\text{H}_4)]^+$, 135480-81-8; $[(\text{C}_6\text{Me}_6)\text{FeCp}]^{2+}$, 135480-82-9; (cymene)Ru($\text{Et}_2\text{C}_2\text{B}_4\text{H}_4$)⁺, 135512-57-1; $[(\text{C}_6\text{H}_6)\text{Ru}(\text{Et}_2\text{C}_2\text{B}_4\text{H}_4)]^+$, 120771-71-3; $[(\text{C}_6\text{Me}_5\text{H})\text{Fe}(\text{Et}_2\text{C}_2\text{B}_4\text{H}_4)]^-$, 135480-84-1; $[(\text{C}_6\text{Me}_4\text{H}_2)\text{Fe}(\text{Et}_2\text{C}_2\text{B}_4\text{H}_4)]^-$, 135480-85-2; $[(1,3,5\text{-C}_6\text{Me}_3\text{H}_3)\text{Fe}(\text{Et}_2\text{C}_2\text{B}_4\text{H}_4)]^-$, 135480-86-3; $[(1,4\text{-C}_6\text{Me}_2\text{H}_4)\text{Fe}(\text{Et}_2\text{C}_2\text{B}_4\text{H}_4)]^-$, 135480-87-4; $[(\text{C}_6\text{MeH}_5)\text{Fe}(\text{Et}_2\text{C}_2\text{B}_4\text{H}_4)]^-$, 135480-88-5; $[(\text{C}_6\text{H}_6)\text{Fe}(\text{Et}_2\text{C}_2\text{B}_4\text{H}_4)]^-$, 135480-89-6; Bu_4NPF_6 , 3109-63-5; Pt, 7440-06-4; Hg, 7439-97-6; CH_2Cl_2 , 75-09-2.

(26) The oxidation of $[(\eta^6\text{-benzene})\text{FeCp}^*]^+$ is also irreversible; $E_p = +0.84$ V versus ferrocene: Brown, K. N.; Field, L. D.; Lay, P. A.; Lindell, C. M.; Masters, A. F. *J. Chem. Soc., Chem. Commun.* 1990, 408.

(27) In a brief unpublished study in 1975 at the University of Vermont, Mr. Al Bijunas showed that the zwitterionic complex $\text{CpFe}[\eta^6\text{-C}_6\text{H}_5(\text{BPh}_3)]$ undergoes a one-electron oxidation having partial chemical reversibility with $E^\circ = +0.60$ V versus Fc in CH_3CN . The sample was provided to WEG by Drs. David Owen and Donald Slocum.