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Structural, Spectroscopic, and Electrochemical Studies of Edge-Bridged Open Ferrocenes

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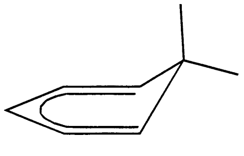
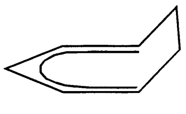
The edge-bridged open ferrocenes, Fe(dmch)$_2$ (**1**), Fe(c-C_7H_9)$_2$ (**2**), and Fe(c-C_8H_{11})$_2$ (**3**, dmch = dimethylcyclohexadienyl; c-C_7H_9 = cycloheptadienyl; c-C_8H_{11} = cyclooctadienyl) are more readily oxidized than ferrocene by ca. 460−680 mV, the ease of oxidation increasing with ring size. The kinetic stabilities of the 17-electron cations follow a trend that is opposite to their thermodynamic ease of formation. ESR measurements show that the cations are low spin, suggesting a mainly Fe($3d_{z^2}$) SOMO. The cation Fe(dmch)$_2^+$ was isolated as a deep green [Fe(dmch)$_2$][B(C_6H_5)$_4$] salt. Both the neutral and cationic forms of Fe(dmch)$_2$ have been studied by X-ray diffraction, thereby allowing for structural comparisons of the two species. In particular, the oxidation of the 18-electron Fe(dmch)$_2$ complex leads to the adoption of a nearly staggered conformation, similar to what was previously found only for early metals such as titanium and vanadium. As in the case of ferrocene, oxidation is accompanied by an increase in the average Fe−C bond distance.

Introduction

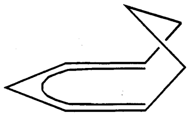
One of the classic properties of ferrocene is its reversible oxidation to the deep-blue, low-spin ferrocenium cation,[1a] Fe(C_5H_5)$_2^+$. Due to the reversibility of this process, and the high stabilities of the two species, the Fe(C_5H_5)$_2$/Fe(C_5H_5)$_2^+$ redox couple has become a convenient and commonly employed electrochemical standard.[1b−d] Not surprisingly, then, once a series of bis(pentadienyl)iron, or open ferrocene, complexes was reported,[2] their electrochemical behavior became of interest. In fact, it was found that Fe(2,4-C_7H_{11})$_2$ (C_7H_{11} = dimethylpentadienyl) was oxidized more readily than ferrocene by ca. 0.38 V, although reversibility of this process required low temperatures.[3] There are reasons to expect that open ferrocenium ions, as well as pseudoferrocenium ions,[4] derived from *edge-bridged* pentadienyl ligands such as 6,6-dimethylcyclohexadienyl (dmch), cycloheptadienyl (c-C_7H_9), and cyclooctadienyl (c-C_8H_{11}) will exhibit greater kinetic, and perhaps thermodynamic, stabilities compared to Fe(2,4-C_7H_{11})$_2^+$. First, the edge-bridges themselves should impart some thermodynamic stabilization, as occurs upon alkylation of metallocene systems.[5] In addition, the decomposition of Fe(2,4-C_7H_{11})$_2^+$ occurs via a ligand-coupling process,[6] and it has been demonstrated that at least the dmch (6,6-dimethylcyclohexadienyl) ligand is much less prone to undergo coupling reactions than are other pentadienyl ligands.[7] Thus, while η^5-bound pentadienyl ligands rarely even lead to stable complexes with first row transition metals in the +3 oxidation state,[8] the dmch ligand does form a stable complex with titanium in the +4 oxidation state.[9] The compound Fe(dmch)$_2$ has, in fact, been stated to undergo a reversible oxidation at room temperature on the e-chem time scale.[10]



dmch



c-C_7H_9



c-C_8H_{11}

We wish to report a detailed examination of the electrochemical behavior of edge-bridged open fer-

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Table 1. X-ray Data Collection Parameters for $Fe(dmch)_2$ and $Fe(dmch)_2B(C_6H_5)_4$

empirical formula	$FeC_{16}H_{22}$	$FeBC_{40}H_{42}$
mol wt	270.2	589.4
space group	$P2_12_12$	$P2_1$
a (Å)	7.5081(4)	9.9006(2)
b (Å)	8.2790(3)	10.4128(2)
c (Å)	11.1798(5)	15.3443(3)
β	90	93.2415(15)
D_{calc} (g/cm^{-3})	1.291	1.239
vol (Å^3)	694.93(5)	1579.36(5)
λ (Å)	0.71073	0.71073
Z	2	2
temp (K)	200	200
μ(Mo Kα), cm^{-1}	10.61	5.04
2θ range	4.5−33.1	3.3−30.0
data collected (h, k, R)	11, 12, 17	−13, +12; −14, +10; 21
no. of reflns collected	2592	6585
no. of independent obsd reflns ($F_o > 2\sigma(F_o)$)	2258	5947
$R(F)$	0.0507	0.0409
$R(wF)$	0.1109	0.0910
N_o/N_v	22.4	14.0
GOF	1.05	1.10
eÅ^{-3}	0.80/−0.61	0.67/−0.35

rocenes containing the dmch, cycloheptadienyl, or cyclooctadienyl ligands, along with structural studies which provide additional insight into the changes that take place as a result of their one-electron oxidation processes.

Experimental Section

All syntheses and manipulations of compounds were carried out under a nitrogen atmosphere, using Schlenk techniques or a glovebox. $Fe(dmch)_2$ (**1**), $Fe(c\text{-}C_7H_9)_2$ (**2**), $Fe(c\text{-}C_8H_{11})_2$ (**3**), and $[Fe(dmch)_2][B(C_6H_5)_4]$ were prepared as previously described.[11] Electrochemical experiments were performed on a PAR 173 potentiostat with a Model 276 interface in an inert atmosphere of dinitrogen. The working electrode employed for cyclic voltammetry (CV) and linear scan voltammetry (LSV) was either a 1.5-mm-diameter glassy carbon or 2-mm-diameter platinum disk that was polished with 1-μm and 0.25-μm Metadi II diamond polishing compound (Buehler), rinsed with deionized water, and dried under vacuum and nitrogen prior to use. Bulk electrolyses were performed at a Pt basket electrode in a standard H-configuration cell with working, auxiliary, and reference electrode compartments separated by fine-porosity frits. Dichloromethane distilled over CaH_2 was further purified by 3 freeze−pump−thaw cycles followed by vacuum distillation immediately prior to use. Analyte concentrations were approximately 1 mM and supporting electrolyte concentrations were between 0.05 and 0.1 M. Tetrabutylammonium hexafluorophosphate, $[NBu_4][PF_6]$, and tetrabutylammonium tetrakis(perfluorophenyl)borate, $[NBu_4][B(C_6F_5)_4]$,[12] were prepared by water/methanol metathesis between tetrabutylammonium bromide (Aldrich) and ammonium hexafluorophosphate (Elf Atochem) or lithium tetrakis(perfluorophenyl)borate (Boulder Scientific), respectively. ESR experiments were performed on a Bruker 300E spectrometer at ambient temperature and 130 K.

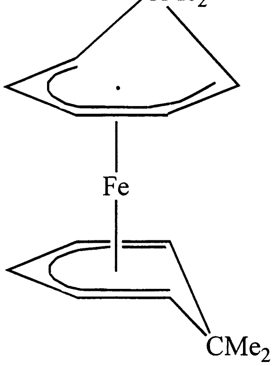
Crystals of **1** and **1**$[B(C_6H_5)_4]$ were obtained by slowly cooling saturated solutions of the compounds in hexane or acetonitrile, respectively. They were then mounted on glass fibers with Paratone oil, and transferred to a Nonius Kappa CCD diffractometer. The structures were each solved by direct methods and difference Fourier maps, using the SIR97 (Release 1.02) and SHELX97 programs. Additional details concerning the crystal data and structural solutions are presented in Table 1.

Table 2. Chemical and Physical Properties of Iron Sandwich Complexes

	compd	$E_{1/2}$ (mV) vs ferrocene	ESR g-values	color of cation in soln
$1^{0/+}$	$Fe(C_6H_5Me_2)_2{}^{0/+}$	−460	2.17, 2.09, 2.02	green
$2^{0/+}$	$Fe(C_7H_9)_2{}^{0/+}$	−495	2.20, 2.08, 2.02	green
$3^{0/+}$	$Fe(C_8H_{11})_2{}^{0/+}$	−680	2.21, 2.06, 2.02	pink

Results and Discussion

Electrochemistry. As found earlier[3] for the open ferrocene $Fe(2,4\text{-}C_7H_{11})_2$, **4** ($C_7H_{11}$ = dimethylpentadienyl), the 6,6′-dimethylcyclohexadienyl compound $Fe(dmch)_2$, **1**, is oxidized more easily than ferrocene (Table 2, $E_{1/2} = -0.46$ V vs Cp_2Fe). The same is found for the cycloheptadienyl compound $Fe(c\text{-}C_7H_9)_2$, **2** ($E_{1/2} = -0.49_5$ V), and the cyclooctadienyl compound $Fe(c\text{-}C_8H_{11})_2$, **3** ($E_{1/2} = -0.68$ V). In cyclic voltammetry experiments, the oxidations of all three compounds were found to be quasi-Nernstian one-electron processes giving monocations that were stable on the CV time scale (Figure 1). The fact that ΔE_p values in CV scans essentially mimicked those of ferrocene under similar experimental conditions implies that the heterogeneous electron-transfer processes of the one-electron oxidations are quite rapid, a conclusion that is supported by the rather small structural changes observed between **1** and **1**$^+$ (see below). When $[NBu_4][PF_6]$ was used as the supporting electrolyte in CV scans of compounds **2** and **3**, anomalies (specifically, irreproducible scans and broadened waves) attributable to electrode fouling[13] were observed.



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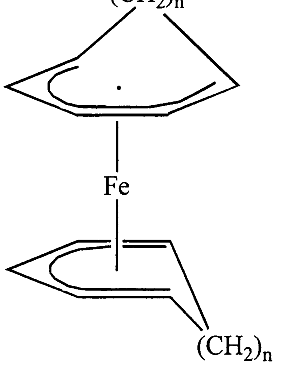
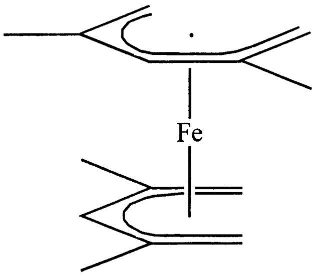


2 (n = 2); **3** (n = 3)



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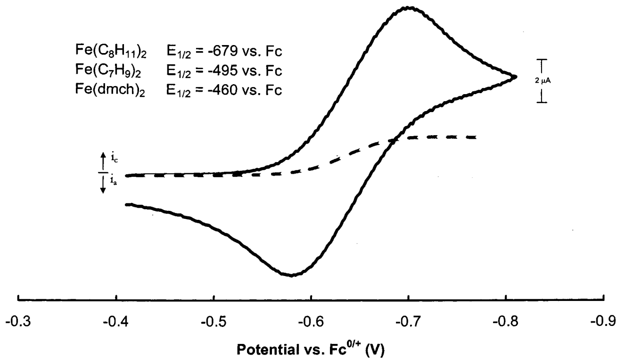

Figure 1. Typical electrochemistry exhibited by the cyclic pentadienyl Fe(III) complexes. The data are of 1.5 mM $\mathbf{2}^{+/0}$ in CH_2Cl_2/0.07 M $[NBu_4][B(C_6F_5)_4]$ at 230 K. Scan rates: CV, 200 mV/s; LSV, 1 mV/s. The LSV (dashed line) has only cathodic currents, showing that the analyte ($\mathbf{2}^+$) is exclusively in the oxidized form. The rather large CV ΔE_p value (~130 mV) is due to solution resistance. At room temperature the ΔE_p value was about 70 mV.

A diffusion constant of 6.2×10^{-6} cm^2 s^{-1} was measured by chronoamperometry for **1** in CH_2Cl_2/0.1 M $[NBu_4][B(C_6F_5)_4]$. The anodic processes are described in eq 1:

$$\mathrm{Fe}(\eta^5\text{-cyclodienyl})_2 \rightleftharpoons \mathrm{Fe}(\eta^5\text{-cyclodienyl})_2^{\,+} + e^- \quad (1)$$

$E_{1/2}$ values become increasingly negative as one goes from **1** to **2** to **3**. A detailed quantitative comparison is clouded by the presence of a bridging CMe_2 group in the ligand of **1**, in contrast to the exclusively CH_2 bridging groups in **2** and **3**. It is reasonable to assume, however, a value of −0.1 V for each substitution of a CH_2 group by a CMe_2 group in **1**. In this way an adjusted value of $E_{1/2} = -0.30$ V is obtained as an estimate for oxidation of the metastable compound Fe(*c*-$C_6H_7)_2$.[10b] Comparison with the values measured for **2** and **3** leads to the conclusion that the Fe(III) oxidation state is progressively stabilized by ca. 190 mV each time the cyclic ligand is increased in size by a single CH_2 unit.

Bulk electrolysis experiments indicated that the most long-lived Fe(III) cation of the series is $\mathbf{1}^+$, for which there is virtually quantitative regeneration of **1** when solutions of the former are cathodically re-electrolyzed at room temperature. It was found that the approximate half-life of $\mathbf{2}^+$ was 30 min at room temperature, and that a reduced temperature of ca. 230 K was necessary to generate persistent electrolysis solutions of $\mathbf{3}^+$. The electron stoichiometry of eq 1 was confirmed by coulometry of the anodic process of **2** at 230 K, which yielded 1.0 F/equiv. As a group, the Fe(III) cyclodienyl cations appear to have greater kinetic stabilities than those observed for open ferrocenium-type ions of noncyclic dienyls. This is perhaps not surprising, given that the open ferrocenium ions have been shown to react by dimerization at the ligand, a process that is less likely in the cyclodienyl analogues.[6]

In the case of **1**, a second oxidation wave was observed. The oxidation of $\mathbf{1}^+$ occurs as an irreversible process of apparent two-electron height with $E_{pa} \cong 1.4$ V vs $Cp_2Fe^{0/+}$. The separation of the first and second oxidations of **1** is therefore approximately 1.8 to 1.9 V, similar to the approximate 1.7 V difference measured for $Cp^*_2Fe^{0/1+/2+}$ and the estimate of 1.6 V for the two oxidation waves of ferrocene itself. Like the oxidation of $\mathbf{1}^+$, that of Cp_2Fe^+ is an irreversible multielectron process.[14]

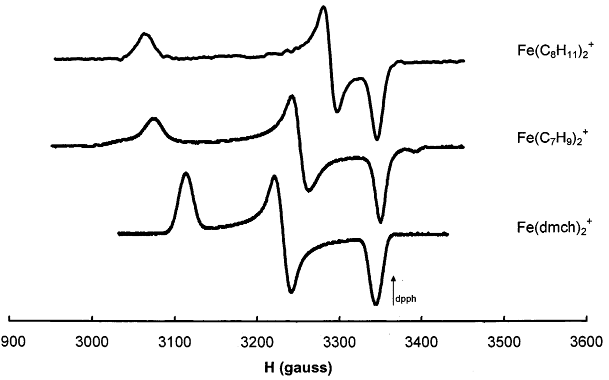

Figure 2. Frozen ESR spectra of the three cyclic-pentadienyl Fe(III) species generated electrochemically. Spectra were acquired in a dichloromethane/$[NBu_4][B(C_6F_5)_4]$ medium at 130 K.

Table 3. Bonding Parameters for Fe(6,6-dmch)$_2$

	Bond Distances (Å)		
Fe−C1	2.108(3)	C1−C2	1.394(4)
Fe−C2	2.050(2)	C2−C3	1.413(5)
Fe−C3	2.057(3)	C3−C4	1.386(5)
Fe−C4	2.035(3)	C4−C5	1.399(5)
Fe−C5	2.093(4)	C5−C6	1.517(5)
C6−C7	1.548(5)	C6−C1	1.494(6)
C6−C8	1.530(5)		
	Bond Angles (deg)		
C1−C2−C3	119.1(3)	C4−C5−C6	119.5(3)
C2−C3−C4	117.9(3)	C5−C6−C1	99.9(3)
C3−C4−C5	119.1(3)	C6−C1−C2	119.4(3)

ESR spectra of the cations $\mathbf{1}^+$, $\mathbf{2}^+$, and $\mathbf{3}^+$ were obtained on the anodic electrolysis solutions. As indicated in Figure 2 and Table 2, spectra based on rhombic **g**-tensors were observed, with all *g*-values being above $g = 2$ and having only small *g*-value anisotropies (a maximum difference of 0.19). In general, these results are as expected for low-spin Fe(III) complexes having a psuedo-sandwich structure of comparatively low symmetry. Elschenbroich et al. have discussed in some detail the ESR spectra observed for open ferrocenium cations,[3] which are very similar to those observed for $\mathbf{1}^+$, $\mathbf{2}^+$, and $\mathbf{3}^+$. On that basis, one may conclude that the SOMO in the Fe(III) cyclodienyl compounds has largely Fe($3d_{z^2}$) character. Because the very ligand-dependent $E_{1/2}$ values for compounds **1**, **2**, and **3** favor a ligand-based HOMO, we conclude that the oxidation process is likely to involve conversion from a ligand-based HOMO in the 18-electron complexes to a metal-based SOMO in the corresponding 17-electron cations. There is ample precedent for this among iron π complexes.[3,15]

Structures of 1 and $\mathbf{1}^+$. The structure of the Fe(II) complex **1** is presented in Figure 2, while pertinent bonding parameters are provided in Table 3. With these

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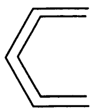
Table 4. Selected Bonding Parameters for Various Open Ferrocenes

parameter	Fe(2,4-C_7H_{11})$_2$[a] (**4**)	Fe(*c*-C_8H_{11})$_2$[b] (**3**)	Fe(*c*-C_7H_9)$_2$[c] (**2**)	Fe(dmch)$_2$ (**1**)	Fe(dmch)$_2^+$ (**1**$^+$)
conf. angle[d]	59.7	58.4	53.9	47.5	87.1
inter lig. tilt	15.0	22.7	13.9	2.4	5.1
C(1)- - -C(5)	2.785	2.947	2.715	2.305	2.402
M−CM[e]	1.508	1.480	1.497	1.569	1.614
M−C[1]	2.094(5)	2.080(3)	2.070(2)	2.108(3)	2.114(2)
M−C[2]	2.085(4)	2.061(3)	2.040(2)	2.050(2)	2.085(2)
M−C[3]	2.084(3)	2.114(3)	2.068(2)	2.057(3)	2.090(4)
M−C[4]	2.062(3)	2.064(3)	2.038(2)	2.035(3)	2.132(2)
M−C[5]	2.122(3)	2.123(3)	2.126(2)	2.093(4)	2.149(3)
M−C (av)	2.089	2.088	2.071	2.068	2.114
C[1]−C[2]−C[3]	124.1(4)	127.7(3)	126.8(2)	119.1(3)	119.8(2)
C[2]−C[3]−C[4]	125.5(3)	125.4(3)	122.8(2)	117.9(3)	119.6(2)
C[3]−C[4]−C[5]	120.7(3)	124.2(3)	119.2(2)	119.1(3)	119.4(2)
C[2]−C[1]−C[6]	(- - -)	126.7(3)	127.0(2), 120.9(1)[f]	119.4(3)	120.4(3)
C−C (deloc.)	1.411	1.412	1.409	1.398	1.396
C[6] tilts[g]	(- - -)	66.9 (52.0)	50.3 (43.6)[h]	28.3 (27.0)	24.7 (20.8)
hydrogen tilts	(- - -)	24.6	15.8	6.8	7.1
fold angle[i]	68.1	70.6	66.4	62.9	65.0

[a] Reference 2. [b] Reference 16. [c] Reference 11. [d] Defined by the angles between the two Fe−C[3]−C[1,5] planes, with C[3] referring to the central carbon atom and C[1,5] being the midpoint between the two terminal carbon atoms. [e] CM = center of mass for the metal-bound carbon atoms. [f] Two values are given since the two bridge carbon atoms experience different tilts. [g] The first value is derived from torsion angles, the second from deviations out of the pentadienyl planes. [h] Due to the bridge asymmetry, these are averages of 46.8° (53.4)° and 53.8° (33.8)° for C(6,13) and C(7,14), respectively. The apparent inversion in the relative degree of tilts arises from the nonplanarity of the dienyl fragment. [i] Defined by the angle between the dienyl plane and the Fe−C[1]−C[5] plane.

data in hand, it becomes possible to draw a number of comparisons between the structures of edge-bridged open ferrocenes derived from six-, seven-, and eight-membered rings (Table 4). First, while the conformation angle of Fe(*c*-C_8H_{11})$_2$ (**3**) is quite close to the expected value of 60° for an idealized gauche-eclipsed structure,[16] one observes a steady decrease from its value of 58.4° to a value of 47.5° for **1**. As the major difference between these edge-bridged dienyls is the separation between their terminal carbon atoms (C1, C5), it would seem likely that these are related. In fact, a similar trend exists for the nonbridged analogues. Thus, Fe(2,3,4-C_8H_{13})$_2$ (C_8H_{13} = trimethylpentadienyl) has both a shorter C1−C5 separation (2.706 vs 2.785 Å) and a smaller conformation angle (55.1° vs 59.7°) than Fe(2,4-C_7H_{11})$_2$.[17] One can note in the gauche-eclipsed structures that there is nearly an octahedral arrangement of the formally charged carbon atoms in the 1, 3, and 5 positions such that the three sites derived from one ligand are staggered relative to those from the other. However, as the C1−C5 separation is decreased (see **5**) there would be a net displacement of the four terminal positions toward each other, especially for C1 and C1′, which would be approaching more of an eclipsing arrangement. This could be offset by a twist toward smaller conformation angles.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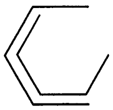
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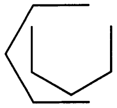
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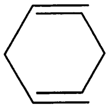
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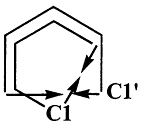

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The C1−C5 separation plays an additional role regarding the M−CM (CM = ligand center of mass, defined by C1−C5) distance. As the former separation increases, geometry requires the dienyl ligands to move closer to a given metal atom to maintain similar M−C distances. Indeed, the Fe−CM distances for the edge-bridged ligands follow the expected trend, which could be extended to include ferrocene itself,[18] for which a bonded C1−C5 separation of ca. 1.40 Å results in an Fe−CM distance of 1.66 Å. The increase in the Fe−CM distance for the smaller rings, together with their tendencies away from eclipsed information, should reduce their inter-ligand steric interactions, and thereby allow for more effective bonding with the metal center, consistent with their given average Fe−C bond distances, and the smaller tilts between their ligand planes. There is indeed other evidence of greater steric demands by the larger edge-bridged ligands, as half-open zirconocenes which incorporate a dmch ligand can be isolated with as many as two phosphine ligands (e.g., Zr(C_5H_5)(dmch)(PMe_3)$_2$), whereas with *c*-C_8H_{11}, only one phosphine ligand can be accommodated.[7] The shorter C1−C5 separations could further promote shorter M−C distances by leading to enhanced metal−ligand overlap (vide infra).

An additional influence of the C1−C5 separation is exerted on the deviations of various substituents from the dienyl ligand planes, defined by the five metal-bound carbon atoms. As can be seen in Table 4, as the C1−C5 separation increases, there is a significant increase in

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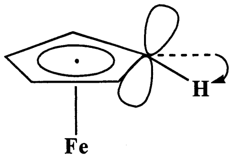
the degree to which the hydrogen atom substituents tilt toward the metal center (cf., 24.6° for **3** vs 6.8° for **1**), and this trend can again be extended to ferrocene itself, for which the smallest tilt is observed, ca. 1.6(4)–3.7(9)°. The tilt for ferrocene has been attributed to an attempt by the C_5H_5 ligands to improve overlap with the small iron center,[19] as in **6**. That the extent of tilting would increase as the girth of the dienyl ligand increases nicely supports the original proposal. Additionally, larger downward tilts by the hydrogen substituents are accompanied by large upward tilts by the attached edge-bridge atoms ("C6"). An assessment of the nature of these tilts is complicated by the fact that they reflect in part not only metal–ligand overlap considerations, but also C–H/π interactions which are generated in at least the dmch and *c*-C_8H_{11} complexes by the tilting of their bridges over the open dienyl ligand, as indicated by upfield chemical shifts of the appropriate bridge hydrogens.[10b,16] The presence of C–H/π interactions is not so apparent for the *c*-C_7H_9 complex in part due to the preference of a C_2H_4 bridge to adopt a lower symmetry orientation to avoid eclipsing interactions between its C–H bonds. A final correlation for the hydrogen tilts (or equivalently, for the C1–C5 separations) may be drawn with the interligand tilts. As the dienyl ligand girth increases, the ligand planes tilt further from a parallel orientation. One could attribute this to increased steric effects as the ligands came closer to one another, thereby promoting each ligand's tilting into the other's open edge. However, it seems more likely that as the dienyl open edge (C1–C5) separations increase, that there would be increasingly unused metal orbital density between them, thereby attracting other metal-bonded atoms to that region.



6

Concerning the differing types of Fe–C bonds in **1**, one generally observes similar trends to those found for the unbridged open ferrocenes such as Fe(2,4-C_7H_{11})$_2$, for which the bonds to the terminal (1,5) positions tended to be longest, and those for the formally uncharged (2,4) positions that tended to be shortest. There is, however, one additional trend evident for the edge-bridged species. One sees that as the ring size increases, from **1** to **3**, there is an increase in the Fe–C3 distance. This might also be a result of the increase in C1–C5 separation, which would require the metal atom to move toward the open edge to maintain a comparable distance from the terminal carbon atoms.

One final comparison of interest concerns the C1–C5 separations for the bridged vs nonbridged species. One can observe that the separation for Fe(*c*-C_7H_9)$_2$ is nearly identical with that for Fe(2,3,4-C_8H_{13})$_2$ (2.715 vs 2.709 Å, respectively), while the separation for Fe(2,4-C_7H_{11})$_2$ is 2.785 Å. Extrapolation to Fe(C_5H_7)$_2$, which unfortunately suffers serious disorder,[20] would suggest a separation close to that in Fe(*c*-C_8H_{11})$_2$. Thus, the cycloheptadienyl and cyclooctadienyl ligands provide good structural analogues for typical nonbridged pentadienyl complexes. On the other hand, dmch thereby is unique, with a much shorter C1–C5 separation that appears responsible for its unique behavior. In fact, dmch has already been revealed from earlier studies to have electronic properties intermediate between those of Cp and pentadienyl ligands,[10b] often giving species with greater stability than any regular pentadienyl analogues, as in the case of **1**$^+$.

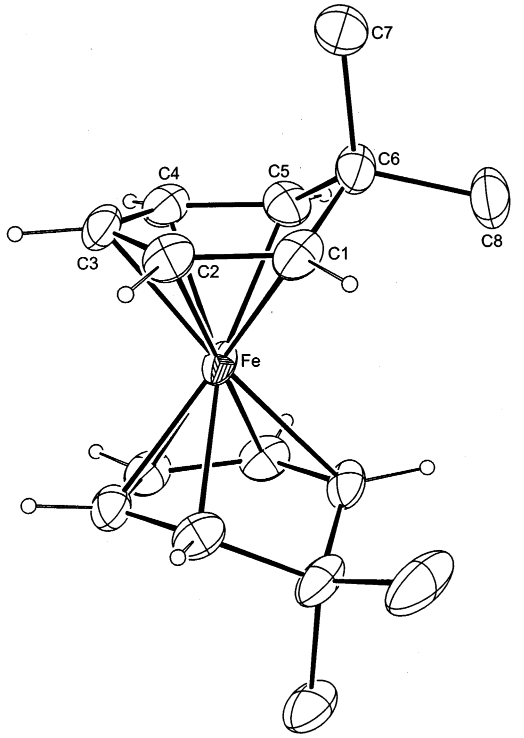


Figure 3. Perspective view and numbering scheme for **1**. The complex has crystallographically imposed C_2 symmetry.

The structural data for **1**$^+$ are presented in Figure 4 and Table 5. These are the first to be obtained for a 17-electron open metallocene, and provide for an interesting comparison with those of its neutral analogue, **1**. One first notes an increase of ca. 0.046 Å in the average Fe–C bond distance upon oxidation, analogous to what has been observed on the oxidation of ferrocene itself.[21] The increase is particularly large for the formally uncharged (2,4) positions. Accompanying this increase is a larger C1–C5 separation, revealing that the dmch ligand, like the 2,4-C_7H_{11} and *c*-C_8H_{11} ligands, will expand itself to improve overlap with larger metal centers.[16,22] The larger C1–C5 separation likely leads to the smaller tilt of the C(CH_3)$_2$ bridge out of the five-membered dienyl ligand plane (24.7° vs 28.2°).

One can also see indications of the size mismatch between the iron and dmch orbitals through the

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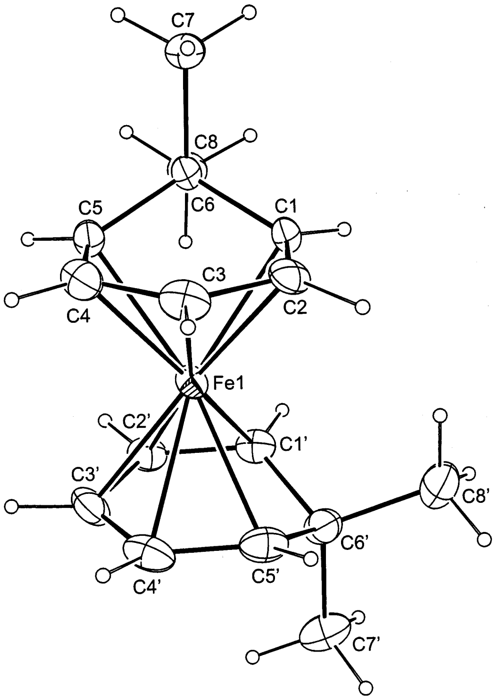

Figure 4. Perspective view and numbering scheme for **1**$^+$.

Table 5. Bonding Parameters for Fe(6,6-dmch)$_2$$^+$B(C$_6H_5$)$_4$$^-$

Bond Distances (Å)			
Fe−C1	2.115(3)	Fe−C1′	2.113(3)
Fe−C2	2.086(3)	Fe−C2′	2.084(3)
Fe−C3	2.101(3)	Fe−C3′	2.078(4)
Fe−C4	2.133(3)	Fe−C4′	2.132(3)
Fe−C5	2.140(3)	Fe−C5′	2.158(3)
C1−C2	1.394(5)	C1′−C2′	1.385(5)
C2−C3	1.412(5)	C2′−C3′	1.426(5)
C3−C4	1.398(5)	C3′−C4′	1.390(5)
C4−C5	1.387(5)	C4′−C5′	1.375(5)
C5−C6	1.510(4)	C5′−C6′	1.526(4)
C6−C1	1.527(4)	C6′−C1′	1.516(4)
C6−C7	1.542(4)	C6′−C7′	1.552(5)
C6−C8	1.531(4)	C6′−C8′	1.528(5)
B−C9	1.647(4)	B−C21	1.640(4)
B−C15	1.638(3)	B−C27	1.637(4)
Bond Angles (deg)			
C1−C2−C3	120.2(3)	C1′−C2′−C3′	119.3(3)
C2−C3−C4	119.2(3)	C2′−C3′−C4′	120.1(3)
C3−C4−C5	119.3(3)	C3′−C4′−C5′	119.5(3)
C4−C5−C6	121.3(3)	C4′−C5′−C6′	121.3(3)
C5−C6−C1	104.0(2)	C5′−C6′−C1′	104.9(2)
C6−C1−C2	119.4(3)	C6′−C1′−C2′	120.0(3)

C1−C6−C5 angles, which average 99.9(3)° and 104.4(2)°, respectively, for the neutral and cationic species. Both values are significantly smaller than the expected ideal tetrahedral value of 109.5°. The value for Fe(dmch)$_2$ is remarkably small, in line with its shorter Fe−C bonds. A somewhat similar trend, though tending to involve larger than normal angles, was also evidenced through structural studies of M(*c*-C$_8$H$_{11}$)$_2$ complexes.[16] Thus, the CH$_2$−CH$_2$−CH$_2$ angle was observed to be smallest for M = Fe (110.6(4)°), and increased to a maximum value of 114.5(7)° for the M = Ti complex.

Clearly of greatest interest is the adoption of a nearly staggered conformation (87.1°). Although a comparably staggered conformation is also adopted by the 15-electron V(2,4-C$_7$H$_{11}$)$_2$ (89.8°),[23] the change of nearly 40° here upon the one-electron oxidation of **1** is very dramatic, especially considering that for the 16-electron Cr(2,4-C$_7$H$_{11}$)$_2$ the conformation angle is 82.2°.[24] One possible explanation for the differing conformational preferences is that for the earlier metal centers, with few d electrons available for δ back-bonding, the bonding might be dominated by π interactions from the two filled, doubly degenerate orbitals available on each ligand to the appropriate empty p$_x$, p$_y$, d$_{xz}$, and d$_{yz}$ orbitals of the metal. This would naturally lead to a preference for the 90° conformation as half of the metal and ligand orbitals mentioned would be aligned with the x axis (and in the xz plane), while the other half would be aligned with the y axis (and in the yz plane). However, as one proceeds to metals with greater d electron occupancies, one could expect δ back-bonding interactions to increase, perhaps thereby favoring the eclipsed conformation. On the other hand, the formal oxidation to Fe^{3+} would clearly be expected to drastically reduce any back-bonding, in accord with the sudden change to a staggered structure. Although this would make for a nice analogy to multiply bonded dimetallic species,[25] there are reasons to think that this could be too simplistic. For example, if one compares the C−O stretching frequencies or force constants of Cr(CO)$_6$ and Ni(CO)$_4$, one finds that they are lower for Cr(CO)$_6$, despite the fact that as one goes from the chromium to the nickel complex, there is a substantial increase in the ratio of the metal d electrons to the number of carbonyl ligands.[26] Hence, back-bonding interactions do not necessarily increase as a metal center acquires more valence electrons, as an increase in the effective nuclear charge for a late metal center may substantially retard back-bonding. Obviously, however, one must also consider which orbitals are being occupied by any additional metal valence electrons, and this is a difficult issue to address for the open metallocenes due to their complex molecular orbital interactions.[27] So, whether it really is δ bonding or the preference for a more octahedral orientation of the formally charged carbon atoms (or some other factor) that leads to the gauche-eclipsed structure of the open ferrocenes remains an open question.

Summary

While the oxidation of a simple open ferrocene has been known for some time to be quite facile, the rapidity of its subsequent decomposition prevented detailed analyses of its properties. The incorporation of edge-bridges, however, leads to a dramatic increase in kinetic stability, even resulting in Fe(dmch)$_2$$^+$ being stable at

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room temperature. It can be expected that oxidation of the more highly methylated pseudo-ferrocenes[4] would be even more favorable. Surprisingly, Fe(dmch)$_2^+$ was found to adopt an 87°, virtually staggered, conformation—something previously only observed for early transition metals. Although one might attribute the preference for such a conformation to a dominance of π ligand-to-metal donation, there is clearly a need for theoretical studies, which might provide a more definitive explanation. Despite the fact that the Fe(c-C_7H_9)$_2^+$ and Fe(c-C_8H_{11})$_2^+$ ions are less thermally stable than Fe(dmch)$_2^+$, it does seem possible that they will also prove isolable at low temperatures. Attempts are underway to further characterize these species.

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Supporting Information Available: Tables giving positional coordinates, anisotropic thermal parameters, and additional bonding parameters for Fe(6,6-dmch)$_2$ and [Fe(6,6-dmch)$_2$][B(C_6H_5)$_4$]. This material is available free of charge via the Internet at http://pubs.acs.org.

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