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

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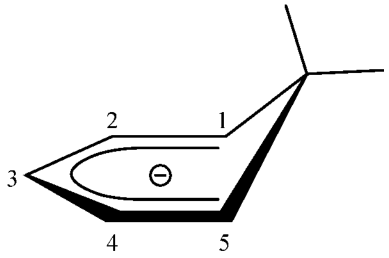
The syntheses of the new compounds Fe(3-Me_3Si-6,6-dmch)$_2$, **2**, and Fe[3-(*i*-Pr)$_3$Si-6,6-dmch]$_2$, **3**, are reported, along with X-ray structural studies of these species, and of the previously reported Fe(1,3,5,6-temch)$_2$ (dmch = dimethylcyclohexadienyl; temch = tetramethylcyclohexadienyl). Each species crystallized in something close to the expected gauche-eclipsed conformation. In accord with previous work on Fe(6,6-dmch)$_2$, but in contrast to results for open ferrocenes such as Fe(2,4-C_7H_{11})$_2$ (C_7H_{11} = dimethylpentadienyl), the three species under study undergo reversible one-electron oxidations at room temperature to stable 17-electron cations, with potentials for oxidation being more favorable than that for ferrocene by 0.51–0.78 V. The edge-bridged open ferrocenes also react in a 1:1 ratio with TCNE (TCNE = tetracyanoethylene), yielding salts that were shown spectroscopically to contain the expected cationic 17-electron metal complexes and the TCNE radical anion.

Introduction

Since the first reports of ferrocene in 1951, the chemistry and physical properties of this and related species have been studied in great detail.[1] One of its most highly utilized properties is its reversible one-electron oxidation to the 17-electron ferrocenium cation.[1,2] Subsequent to the reports of ferrocene, several "pseudo-"[3] and "open-ferrocene"[4] complexes have been reported, containing, respectively, various cyclic and acyclic, but nonaromatic, dienyl ligands. The cyclic analogues include ligands such as cyclo-hexadienyl, -heptadienyl, -octadienyl, and various methylated derivatives, while the acyclic analogues include pentadienyl, 3-methylpentadienyl, 2,4-dimethylpentadienyl, and related species. To date, electrochemical measurements have indicated that although the electronically open iron compounds are all more readily oxidized than ferrocene, the thermal stabilities of their 17-electron cations can be rather limited, especially for the acyclic ligand complexes. In fact, previously the only 17-electron "pseudo" or "open" ferrocenium cation to be isolated at room temperature has been [Fe(6,6-dmch)$_2$]$^+$ (dmch = dimethylcyclohexadienyl),[3e,5a] although a decamethyl[5b] as well as $SiMe_2$- and $SnMe_2$-bridged[3j] analogues have also been observed electrochemically and might well also be isolable. This stability is likely due, at least in part, to the relatively short intertermini (C1--C5) separations that result from the edge-bridges. With a longer C1--C5 separation, and the resulting poorer metal–ligand overlap,[6] the nonbridged open ferrocenes undergo intramolecular coupling reactions. Although the edge-bridge in Fe(6,6-dmch)$_2$ is sufficient to allow the isolation of its one-electron oxidation product, incorporation of additional substituents in the C3 position has been utilized in the species studied herein in order to further impede coupling reactions,[7] which could potentially occur between the nonaromatic dienyl ligands and other π-systems.



6,6-dmch

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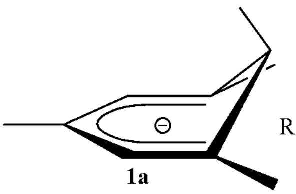
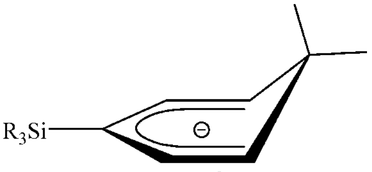
The structures of these species are of relevance to their redox properties. Although ferrocene itself undergoes only a slight breathing upon oxidation, reflected by a slight increase in iron−carbon bond distances,[8] the greater conformational richness of the reduced symmetry (typically C_2) pseudo and open metallocenes raises the possibility of greater redox-initiated structural changes (e.g., the complex Fe(6,6-dmch)$_2$ undergoes a change of some 40° in conformation angle upon oxidation[3e]). We were interested in adding to our knowledge of the structural and redox properties of these systems and in probing their abilities to form complexes or salts with accepting π-systems such as TCNE (TCNE = tetracyanoethylene). A large number of such complexes have been reported with metallocenes acting as the donors, and some have been shown to have interesting electronic or magnetic properties.[9a] This paper reports on our initial findings along these lines and probes the effect of silyl substitutions on the redox potentials of pseudoferrocene compounds. Whereas ferrocene forms a charge-transfer adduct with TCNE,[9b] the significantly lower potentials of substituted pseudoferrocenes incorporating the 1,3,5,6-temch (1,3,5,6-tetramethylcyclohexadienyl, **1a**) or silylated 6,6-dmch (**2a**, **3a**) ligands lead to the formation of true salts, involving 17-electron cations and the TCNE radical anion.



1a



R = Me (**2a**)
i-Pr (**3a**)

Experimental Section

Reactions and procedures were carried out under purified nitrogen. Preparations of neutral iron complexes were carried out using Schlenk methods, whereas those involving formation of 17-electron cations utilized a Vacuum Atmospheres drybox. Hydrocarbon and aromatic solvents used for synthetic purposes were purified using activated alumina columns under nitrogen, while THF was purified by distillation from sodium benzophenone ketyl. 3-Trimethylsilyl-6,6-dimethylcyclohexa-(1,3 or 1,4)-diene can be prepared by a reported procedure[10] or by the reaction of Me$_3$SiCl with K(6,6-dmch).[11] The 3-tris(isopropyl)silyl analogue may be prepared similarly (*vide infra*). The dienes may then be converted to their potassium salts by a reported procedure.[12] Fe(1,3,5,6-temch)$_2$, Fe(**1a**)$_2$ (**1**), was prepared by a published procedure,[3c] though the yields were often substantially lower than reported.

Elemental (C, H) analyses were obtained from Complete Analysis Laboratories, Inc., or Robertson Laboratories.

Bis(3-trimethylsilyl-6,6-dimethylcyclohexadienyl)iron, Fe(3-Me$_3$Si-6,6-dmch)$_2$, Fe(2a)$_2$ (2). To FeCl$_2$(THF)$_2$[3i,13] (0.16 g, 5.9 mmol) at −78 °C was added 20 mL of THF. This was stirred 5 min. To this was added K(3-Me$_3$Si-6,6-dmch) (0.25 g, 11 mmol) in 20 mL of THF, dropwise. Immediately the color changed to a deeper red, and after the mixture was warmed to room temperature over a period of 1 h, the THF was removed *in vacuo*. The solid was extracted using hexanes and was filtered through a Celite pad on a coarse frit. Upon saturation by removal of most of the hexanes *in vacuo* and cooling to −30°, 0.11 g (45%) of the Fe(3-Me$_3$Si-6,6-dmch)$_2$ crystallized in a form suitable for an X-ray diffraction study. ^{1}H NMR (benzene-d_6, ambient): δ 4.37 (d, 2H, H-2,4, J = 6.3 Hz), 2.93 (d, 2H, H-1,5, J = 6.3 Hz), 1.30 (s, 3H, Me), 0.27 (s, 3H, Me), 0.24 (s, 9H, TMS). ^{13}C NMR (benzene-d_6, ambient): δ 85.8 (dd, 2C, C-2,4, J = 161, 8.0 Hz), 77.8 (s, 1C, C-3), 50.5 (broad d, 2C, C-1,5, J = 160 Hz), 34.2 (q, 1C, Me, J = 124.5 Hz), 33.4 (s, 1C, C-6), 30.1 (q, 1C, Me, J = 124 Hz), −0.15 (q, 3C, TMS, J = 118 Hz). MS (EI, 17 eV) [m/z(relative intensity)]: 415(8), 414(22), 401(12), 400(25), 399(100), 397(6), 385(8), 384(25), 220(22), 149(10). Anal. Calcd for FeSi$_2$C$_{22}$H$_{42}$: C, 63.15; H, 10.05. Found: C, 63.44; H, 9.77.

Bis[3-Tris(isopropyl)silyl-6,6-dimethylcyclohexadienyl]iron, Fe[3-(*i*-Pr)$_3$Si-6,6-dmch]$_2$, Fe(3a)$_2$ (3). To K(6,6-dmch) (3.8 g, 26 mmol) at 0 °C in 30 mL of ether was added triisopropylsilyl chloride (5.0 g, 26 mmol) in 10 mL of ether, dropwise over several minutes. This was allowed to stir at room temperature for 2 days and thereafter was quenched with a few drops of water. The mixture was filtered through Celite, and the solution was dried over MgSO$_4$, filtered, and concentrated by rotoevaporation. The crude diene was then taken to the next step.

To KO-*t*-Bu (1.81 g, 16.2 mmol) at 0 °C was added 30 mL of hexanes. This was stirred 5 min, and then *n*-BuLi (7.1 mL, 2.5 M, 18 mmol) was added via syringe. This was stirred an additional 5 min, and the above-prepared diene (4.65 g, 17.8 mmol) in ca. 20 mL of hexanes was added slowly, dropwise, over several minutes. Initially there was no color, but overnight it turned orange. Upon filtering, the solid precipitate, K[3-(*i*-Pr)$_3$Si-6,6-dmch] (4.07 g, 52% yield from Kdmch), went nearly white. This was dried *in vacuo* and stored in a glovebox.

To FeCl$_2$(THF)$_2$ (0.50 g, 1.8 mmol) at −78 °C was added 20 mL of THF. To this was added dropwise, after 5 min of stirring, K[3-(*i*-Pr)$_3$Si-6,6-dmch] (1.05 g, 3.50 mol) in 20 mL of THF. The color changed rapidly to a deep red, and after the mixture was warmed over a period of 1 h to room temperature, the THF was removed *in vacuo*. The solid was extracted using hexanes and was filtered. The Fe[3-(*i*-Pr)$_3$Si-6,6-dmch]$_2$ (0.78 g, 39%) readily crystallized from solution at −30 °C, producing crystals suitable for an X-ray diffraction study. ^{1}H NMR (benzene-d_6, ambient): δ 4.54 (d, 2H, H-2,4, J = 6 Hz), 4.30 (sep, 3H, CH-*i*Pr, J = 6 Hz), 3.08 (s broad, 2H, H-1,5), 1.35 (s, 3H, Me), 1.23 (d, 18H, CH$_3$-*i*Pr, J = 3 Hz), 0.31 (s, 3H, Me). ^{13}C NMR (benzene-d_6, ambient): δ 87.6 (dd, 2C, C-2,4, J = 161 Hz, 8.1 Hz), 75.9 (s, 1C, C-3), 49.4 (v br d, 2C, C-1,5, J = 162 Hz), 33.9 (q, 1C, Me, J = 124.6 Hz), 33.1 (s, 1C, C-6), 30.1 (q, 1C, Me, J = 124 Hz), 19.9 (q, 6C, CH$_3$-*i*Pr, J = 125 Hz), 12.9 (d, 3C, CH-*i*Pr, J = 118 Hz). MS (EI, 20 eV) [m/z (relative intensity)]: 583(10), 582(23), 569(14), 568(46), 567(100). Anal. Calcd for FeSi$_2$C$_{34}$H$_{66}$: C, 69.62; H, 11.26. Found: C, 69.68; H, 11.10.

X-ray Diffraction Studies. Single crystals of the compounds were obtained by cooling their concentrated solutions in hydrocarbon solvents. The crystals were examined under Paratone oil and mounted on glass fibers, which were then transferred to the diffractometer and cooled with a cold stream of nitrogen gas. Each

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(8) (a) An accurate value for the change in the Fe−C distance for ferrocene/ferrocenium is somewhat open to question, as the structure determinations are often plagued by substantial libration of the Cp ligands. An oxidative lengthening of ca. 0.04 Å seems reasonable, based on structural data of Fe(C$_5$H$_4$SiMe$_3$)$_2$ and its cation: Foucher, D. A.; Honeyman, C. H.; Lough, A. J.; Manners, I.; Nelson, J. M. *Acta Crystallogr.* **1995**, *C51*, 1795. (b) For ferrocene/ferrocenium see: Seiler, P.; Dunitz, J. D. *Acta Crystallogr.* **1979**, *B35*, 1068. (c) Martinez, R.; Tiripicchio, A. *Acta Crystallogr.* **1990**, *C46*, 202.

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structure was initially solved by a combination of heavy atom and direct methods using the SIR 97 programs and then subsequently refined using SHELX97.[14] For **3**, the hydrogen atoms were located and subjected to isotropic refinement, while for **1** and **2** they were allowed to ride on their carbon atoms. All other atoms were refined anisotropically. Crystals of **1** were of relatively poor quality and contained four independent molecules, each with a similar structure. Two independent but similar molecules were found for **2**.

Electrochemistry. The experimental reference electrode was a silver/silver chloride wire separated from the working electrode compartment by a fine frit. It was prepared by deposition of AgCl onto silver. Standard three-electrode cells were used, with Pt wire counterelectrodes. The ferrocene/ferrocenium potential was determined by addition of ferrocene at an appropriate time in each experiment, and all potentials in this paper are referred to $FeCp_2^{0/+}$ with a precision of 10 mV. The working electrode for cyclic voltammetry (CV) and linear scan voltammetry (LSV) was a 2 mm diameter glassy carbon disk (Bioanalytical Systems), which had been progressively polished with Metadi II diamond polishing compounds, rinsed with nanopure water, and dried under vacuum prior to use. Bulk electrolyses were conducted using a Pt basket electrode that was treated with nitric acid, washed with nanopure water, and dried at 110 °C. A PAR 273A potentiostat interfaced to a personal computer was used for voltammetry and electrolysis. Analyte concentrations were generally on the order of 1 mM. The supporting electrolyte was 0.05 M $[NBu_4][B(C_6F_5)_4]$, the preparation and properties of which have been described.[15] Dichloromethane was first distilled from CaH_2 and then purified by three freeze–pump–thaw cycles followed by distillation under static vacuum to a flask that was opened in the drybox, in which all the electrochemistry was performed. ESR measurements were performed on a Bruker 300E spectrometer at a temperature of 77 K.

Preparation of TCNE Salts. The 1:1 salts [**1**][TCNE], [**2**][TCNE], and [**3**][TCNE] were prepared using identical procedures from equimolar amounts of the neutral iron complexes and TCNE in benzene. For example, after dissolving complex **2** (8.8 mg, 21 μmol) in 1.5 mL of benzene, this solution was added slowly with stirring to 2.7 mg (21 μmol) of TCNE in 1 mL of benzene. An immediate color change from red-orange to yellow-orange occurred, and a light orange precipitate appeared. The resulting mixture was kept cold (10 °C) and filtered to remove the precipitated TCNE salt, [**2**][TCNE], which was then washed several times with cold benzene. Vacuum evaporation provided 7.5 mg (65%) of analytically pure orange powder, [**2**][TCNE]. Similar procedures for **1** and **3** gave 68% ([**1**][TCNE]) and 60% ([**3**][TCNE]). Anal. Calcd for $C_{28}H_{38}N_4Si_2Fe$ ([**2**][TCNE]): C, 61.96; H, 7.07; N, 10.33. Found: C, 62.27; H, 7.08; N, 10.45. Anal Calcd for $C_{26}H_{30}N_4Fe$ ([**1**][TCNE]): C, 68.71; H, 6.67; N, 12.33. Found: C, 68.17; H, 6.32; N, 12.57. Anal. Calcd for $C_{40}H_{62}N_4Si_2Fe$ ([**3**][TCNE]): C, 67.56; H, 8.81; N, 7.88. Found: C, 67.79; H, 8.74; N, 7.57.

Results and Discussion

Syntheses and Structures. The syntheses of the new silylated open ferrocenes $Fe(3\text{-}R_3Si\text{-}6,6\text{-}dmch)_2$ (R = Me, *i*-Pr) were accomplished straightforwardly in reasonable, unoptimized yields via the reaction of a solvated ferrous chloride derivative with 2 equiv of the appropriate anion, as indicated in eq 1. The deep red complexes are very soluble in organic solvents, readily crystallized, and may be handled at least briefly in air.

$$FeCl_2(THF)_2 + 2K(3\text{-}R_3Si\text{-}6,6\text{-}dmch) \rightarrow Fe(3\text{-}R_3Si\text{-}6,6\text{-}dmch)_2 \quad (1)$$

for which R = Me (**2**), *i*-Pr (**3**).

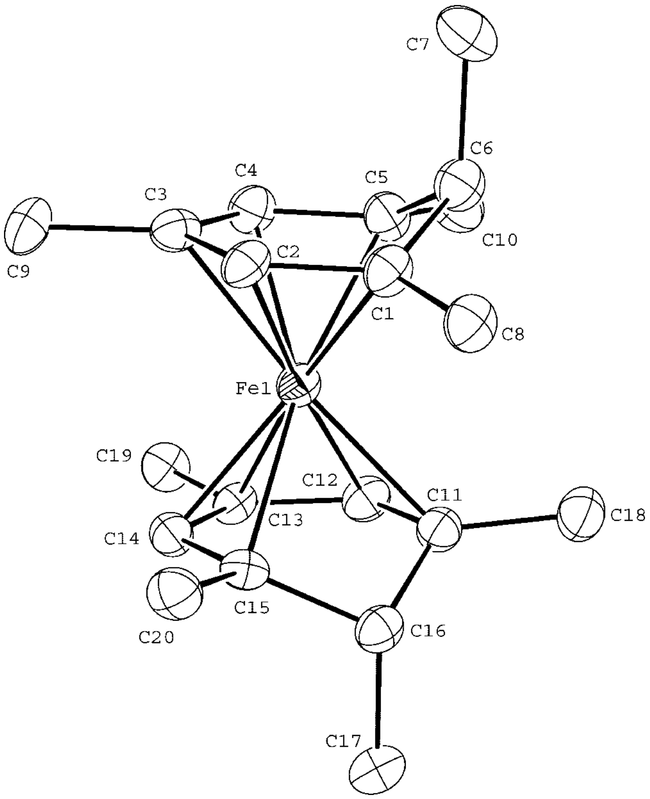
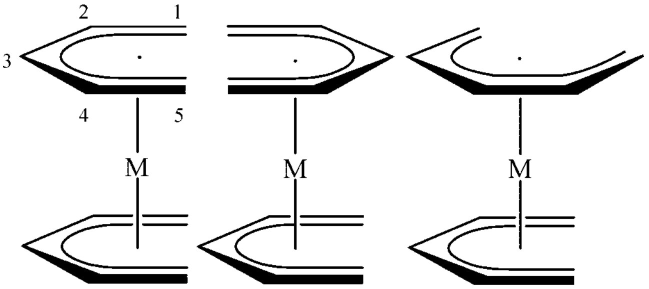


Figure 1. Solid state structure of one of the four independent $Fe(1,3,5,6\text{-}temch)_2$ molecules. All others display similar structures. The 30% probability ellipsoids are shown.

The structure of one of the four independent Fe(1,3,5,6-temch)$_2$ molecules (temch = tetramethylcyclohexadienyl) (**1**) is presented in Figure 1. The relative orientations of the two temch ligands are essentially identical for the four molecules, corresponding to an average twist of 56.8° from the syn-eclipsed (**4**) toward the anti-eclipsed (**5**) open metallocene structures, matching the ca. 60° conformation angle expected for the gauche-eclipsed form **6**.[6] Interestingly, $Fe(6,6\text{-}dmch)_2$ exhibited a conformation angle of only 47.5°, suggesting that the more normal value here may actually be promoted via interligand repulsions between methyl groups.



4 (C_{2v}) **5** (C_{2h}) **6** (C_2)

The Fe−C bond distances ranged from 2.043(6) to 2.138(6) Å, giving an average Fe−C bond distance of 2.085 Å, which can be compared to values of 2.074−2.093 Å in related species.[3]

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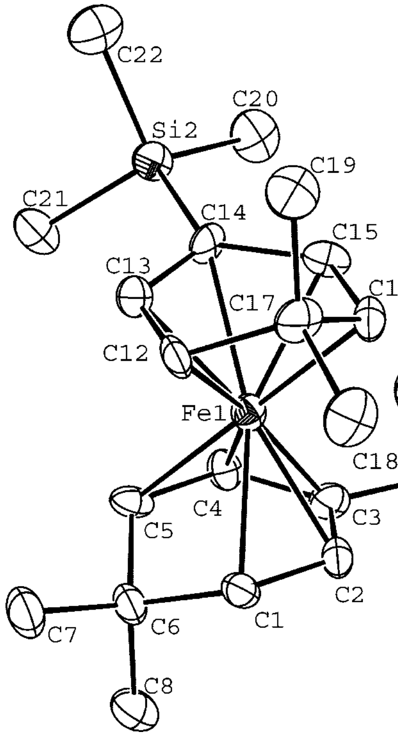

Figure 2. Solid state structure of Fe(3-Me_3Si-6,6-dmch)$_2$. The 30% probability ellipsoids are shown.

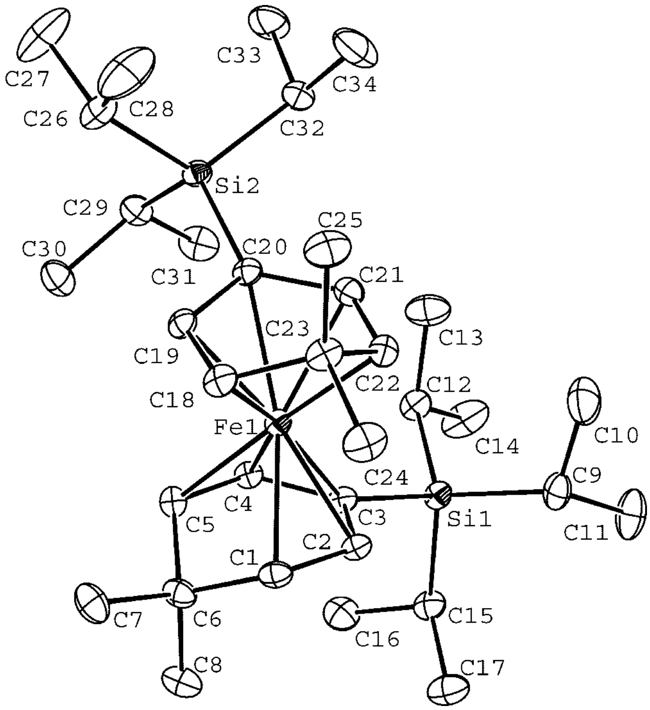

Figure 3. Solid state structure of Fe[3-(*i*-Pr)$_3$Si-6,6-dmch]$_2$. The 30% probability ellipsoids are shown.

As is common in open ferrocenes,[6] the M−C(1,5) distances are longer than those for the C(2–4) atoms. The presence of an alkyl group on the dienyl ligands' central carbon atoms led to the expected contraction in C−C(R)−C bond angle relative to those around the 2 and 4 positions,[6] 116.8(3)° vs 120.1(1)°. The contraction is accompanied by a C[1]--[5] distance of 2.367(2) Å, vs 2.305(8) Å in Fe(6,6-dmch)$_2$. The methyl groups on the delocalized dienyl carbon atoms tilt toward the iron atom, by an average of 5.5° for the terminal and 2.3° for the central carbon atoms. There is an average tilt of 43.5(4)° between the dienyl ligand and C[1]−C[5]−C[6] planes and an average value of 4.7(2)° between dienyl ligand planes. Some distortion of the geometry of the edge-bridge is evidenced by the average value of the C[1]−C[6]−C[5] bond angle, 102.9(2)° (cf., 100.0(3)° in Fe(6,6-dmch)$_2$). The significant reduction of these angles from the ideal tetrahedral value would lead to a shorter C1--C5 separation and to enhanced metal–ligand orbital overlap.

The silyl-substituted compounds (Figures 2 and 3) display several differences relative to their dmch and temch analogues. Perhaps most notably, their conformation angles are unusually large, at 74.6° and 71.0°, respectively, about 25° greater than in Fe(6,6-dmch)$_2$. The average Fe−C bond distances are slightly long at 2.091Å (range 2.039(7)−2.142(8) Å) and 2.100 Å (range 2.060(2)−2.148(2) Å) for the Me_3Si and (*i*-Pr)$_3$Si complexes, respectively. These correlate with increased deviations of their iron atoms from the dienyl ligand planes, 1.577(3) and 1.585(1) vs 1.560(2) Å for Fe(1,3,5,6-temch)$_2$ and 1.558(1) Å for Fe(6,6-dmch)$_2$. The average Fe−C[1,5] distances in a given structure are longest, at ca. 2.13 Å (range 2.103(2)−2.148(2) Å), while the Fe−C[2,4] distances are shortest, at ca. 2.06 Å (range 2.039(7)−2.068(8) Å). The average Fe−C[3] distances range from a minimum of 2.066(3) Å in the temch complex to a value of 2.125(2) Å in the *i*-Pr complex. These values are reasonably consistent with those previously reported for Me_2Si-bridged dmch analogues.[3j−l] There is a greater difference between the dienyl ligands' internal and external C−C bonds, e.g., 1.439(2) vs 1.404(2) Å for those of the *i*-Pr complex, compared to 1.418(2) vs 1.416(2) Å for the temch complex, which could be a result of the stabilization of negative charge brought about by silylation at the 3 position. The silyl-substituted ligands have shorter average C1--C5 separations of 2.317(12) and 2.309(1) Å, arising primarily from their smaller C[2]−C[3]−C[4] angles, which average 114.8(5)° and 114.1(2)° vs 116.8(3)° in the temch complex. This leads to increased distortions in the C1−C6−C5 angles, which average 99.9(3)° and 99.2(1)°, respectively, for the Me- and *i*-Pr-substituted silyl compounds. In contrast to the methyl substituents on the C[3] positions of the temch ligands, the silyl substituents tilt out of their dienyl ligand planes in a direction away from their iron atoms, at 3.6° and 14.5°, respectively. The hydrogen substituents in the *i*-Pt complex could be refined and revealed reasonable average tilts of ca. 9° and 12°, respectively, for the H[1,5] and H[2,4] atoms, toward the iron centers.

Electrochemistry. All three compounds gave essentially Nernstian one-electron oxidations to persistent 17-electron cations. These anodic reactions occurred at relatively facile potentials, with $E_{1/2}$ values of −0.78, −0.51, and −0.53 V (vs $FeCp_2^{0/+}$), respectively, for compounds **1**, **2**, and **3**. Table 5 collects these values as well as those for other relevant bis(cyclohexadienyl)iron compounds. The voltammetric behavior of these systems was quite straightforward, consistent with a chemically reversible, diffusion-controlled, one-electron process with no evidence of electrode adsorption effects. The diagnostic criteria used to make these conclusions are described elsewhere.[16] Although the heterogeneous electron-transfer rates were not determined, no evidence of slow charge transfer was observed, nor is it expected in these systems. CV experiments with scan rates up to about 1 V s^{-1} showed roughly the same ΔE_p values as seen for ferrocene itself.

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(16) Geiger, W. E. In *Laboratory Techniques in Electroanalytical Chemistry*, 2nd ed.; Kissinger, P. T., Heineman, W. R., Eds.; Marcel Dekker: New York, 1996; pp 683–693.

Table 1. X-ray Data Collection Parameters

empirical formula	$FeC_{20}H_{30}$, **1**	$FeSi_2C_{22}H_{38}$, **2**	$FeSi_2C_{34}H_{62}$, **3**
molecular weight	326.29	414.55	582.87
space group	$P2_1/n$	$P2_1/c$	$P\bar{1}$
a (Å)	7.7101(2)	21.7527(12)	9.9956(2)
b (Å)	59.1719(19)	11.3266(7)	11.2121(3)
c (Å)	15.7478(5)	21.7446(11)	17.1629(4)
α (deg)	90	90	94.6290(10)
β (deg)	102.1309(10)	118.717(3)	95.3399(13)
γ (deg)	90	90	115.6132(13)
D_{calc} (g/cm^{-3})	1.234	1.172	1.131
volume (Å^3)	7024.1(4)	4698.6(5)	1711.19(7)
λ (Å)	0.71073	0.71073	0.71073
Z	16	8	2
temp (K)	150	150	150
μ(Mo Kα) (cm^{-1})	8.52	7.47	5.31
2θ range	2.7 – 55.1	2.1 – 54.9	5.0 – 55.0
data collected (h, k, l)	$-10 \le h \le 10$	$-21 \le h \le 27$	$-12 \le h \le 12$
	$-76 \le k \le 76$	$-9 \le k \le 14$	$-14 \le k \le 12$
	$-20 \le l \le 20$	$-28 \le l \le 28$	$21 \le l \le 22$
no. of reflns collected	24 060	13 226	11 940
no. of indep obsd reflns ($F_o > 2\sigma(F_o)$)	14 414	10 168	7725
$R(F)$	0.0834	0.0468	0.0407
$R(wF)$	0.2054	0.0897	0.0972
N_o/N_v	18.2	21.5	13.3
GOF	1.06	1.03	1.04
largest diff peak/hole (e Å^{-3})	0.79/−1.12	0.41/−0.33	0.43/−0.52

Table 2. Pertinent Bonding Distances for Fe[1,3,5,6-temch]$_2$, 1

Fe(1)−C(1)	2.125(6)	Fe(3)−C(1B)	2.123(6)
Fe(1)−C(2)	2.050(6)	Fe(3)−C(2B)	2.054(6)
Fe(1)−C(3)	2.055(6)	Fe(3)−C(3B)	2.069(6)
Fe(1)−C(4)	2.045(6)	Fe(3)−C(4B)	2.046(6)
Fe(1)−C(5)	2.120(7)	Fe(3)−C(5B)	2.130(6)
Fe(1)−C(11)	2.121(6)	Fe(3)−C(11B)	2.120(6)
Fe(1)−C(12)	2.056(6)	Fe(3)−C(12B)	2.060(6)
Fe(1)−C(13)	2.073(6)	Fe(3)−C(13B)	2.075(6)
Fe(1)−C(14)	2.051(6)	Fe(3)−C(14B)	2.066(6)
Fe(1)−C(15)	2.133(6)	Fe(3)−C(15B)	2.134(6)
Fe(2)−C(1A)	2.127(5)	Fe(4)−C(1C)	2.119(6)
Fe(2)−C(2A)	2.056(6)	Fe(4)−C(2C)	2.046(6)
Fe(2)−C(3A)	2.066(6)	Fe(4)−C(3C)	2.054(6)
Fe(2)−C(4A)	2.057(6)	Fe(4)−C(4C)	2.043(6)
Fe(2)−C(5A)	2.138(6)	Fe(4)−C(5C)	2.125(6)
Fe(2)−C(11A)	2.116(6)	Fe(4)−C(11C)	2.114(6)
Fe(2)−C(12A)	2.058(6)	Fe(4)−C(12C)	2.050(6)
Fe(2)−C(13A)	2.068(6)	Fe(4)−C(13C)	2.066(6)
Fe(2)−C(14A)	2.060(6)	Fe(4)−C(14C)	2.062(6)
Fe(2)−C(15A)	2.138(6)	Fe(4)−C(15C)	2.124(6)

Table 3. Pertinent Bonding Distances for Fe[3-Me$_3$Si-6,6-dmch]$_2$, 2

Fe(1)−C(1)	2.142(8)	Fe(2)−C(1A)	2.141(9)
Fe(1)−C(2)	2.043(8)	Fe(2)−C(2A)	2.068(8)
Fe(1)−C(3)	2.112(7)	Fe(2)−C(3A)	2.078(6)
Fe(1)−C(4)	2.064(6)	Fe(3)−C(4A)	2.048(6)
Fe(1)−C(5)	2.125(6)	Fe(2)−C(5A)	2.111(7)
Fe(1)−C(12)	2.136(6)	Fe(2)−C(12A)	2.133(6)
Fe(1)−C(13)	2.058(8)	Fe(2)−C(13A)	2.043(7)
Fe(1)−C(14)	2.072(8)	Fe(2)−C(14A)	2.092(8)
Fe(1)−C(15)	2.039(7)	Fe(2)−C(15A)	2.064(8)
Fe(1)−C(16)	2.114(7)	Fe(2)−C(16A)	2.138(7)

Table 4. Pertinent Bonding Parameters for Fe[3-(*i*-Pr)$_3$Si-6,6-dmch]$_2$, 3

Bond Distances			
Fe−C(1)	2.133(2)	Fe−C(18)	2.148(2)
Fe−C(2)	2.062(2)	Fe−C(19)	2.063(2)
Fe−C(3)	2.121(2)	Fe−C(20)	2.130(2)
Fe−C(4)	2.066(2)	Fe−C(21)	2.060(2)
Fe−C(5)	2.116(2)	Fe−C(22)	2.103(2)
Bond Angles			
C(1)−C(2)−C(3)	120.8(2)	C(18)−C(19)−C(20)	121.0(2)
C(2)−C(3)−C(4)	114.3(2)	C(19)−C(20)−C(21)	113.8(2)
C(3)−C(4)−C(5)	120.3(2)	C(20)−C(21)−C(22)	120.6(2)

Bulk anodic electrolyses carried out at 268 K confirmed the one-electron stoichiometry by releasing 1.1 F/eq, 1.1 F/eq, and 1.0 F/eq for **1**, **2**, and **3**, respectively. Reverse electrolyses in which the 17 e$^-$ cation was rereduced to the neutral starting material were also carried out, and linear scan voltammetry (LSV) was used to quantify the redox products. In all cases, the combined anodic/cathodic electrolyses regenerated essentially all the original neutral complex, demonstrating the quantitative chemical reversibilities of the 18 e$^-$/17 e$^-$ couples. Figure 4 shows the CV and LSV scans of **1**$^+$, which were generated in a bulk anodic electrolysis of 0.8 mM **1**. The colors of the solutions went from the red, orange, and reddish-orange of the neutral compounds to yellow, yellow, and pale orange, respectively, for the cations of **1**, **2**, and **3**. These contrast significantly with the deep blue color of the ferrocenium ion and the deep green color of Fe(dmch)$_2$$^+$.

The $E_{1/2}$ data may be compared with the value of −0.46 V previously reported for Fe(6,6-dmch)$_2$ in addressing the electronic effect of substitution of H by either CH_3 or SiR_3. The simplest comparisons are for **2** and **3**, both of which differ from Fe(6,6-dmch)$_2$ only in the replacement of a single H by a SiR_3 group on each ring. This results in a shift of −25 mV per $SiMe_3$ group or −35 mV per Si(*i*-Pr)$_3$ group, in both cases stabilizing the Fe(III) oxidation state. A larger shift is seen for substitution of H by CH_3. Compound **1** has three additional methyl groups per ring on carbon atoms that are directly bound to the metal. A total shift of −320 mV induced by the six additional methyl groups gives an average of −53 mV per CH_3 substitution. For the sake of comparison with substituted ferrocenes, we note that the potential of decamethylferrocene is −0.61 V vs $FeCp_2^{0/+}$ in this medium, a shift of −61 mV per CH_3 group. Regarding the effect of the $SiMe_3$ group on ferrocene, a shift of +10 mV has been reported.[17] The electrochemical data suggest that there are only rather minor differences in the electronic effects of methyl substitutions in the cyclohexadienyl and cyclopentadienyl

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Table 5. $E_{1/2}$ Potentials in Volts vs $FeCp_2^{0/+}$ for One-Electron Oxidation of Iron Cyclohexadienyl Complexes and Other Redox Processes

compound	$E_{1/2}$	medium	ref
Fe(6,6-dmch)$_2$	−0.46	CH_2Cl_2/0.07 M $[NBu_4][B(C_6F_5)_4]$	3a, 5a
Fe(1,3,5,6-temch)$_2$, **1**	−0.78	CH_2Cl_2/0.05 M $[NBu_4][B(C_6F_5)_4]$	this work
Fe(3-Me_3Si-6,6-dmch)$_2$, **2**	−0.51	CH_2Cl_2/0.05 M $[NBu_4][B(C_6F_5)_4]$	this work
Fe[3-(*i*-Pr)$_3$Si-6,6-dmch]$_2$, **3**	−0.53	CH_2Cl_2/0.05 M $[NBu_4][B(C_6F_5)_4]$	this work
$Fe(C_6Me_6H)(C_6Me_6CH_2Ph)$	−0.95	DMF/0.1 M $[NBu_4][BF_4]$[a]	5b
TCNE/$TCNE^{-1}$	−0.27	CH_3CN/0.1 M $[NBu_4][PF_6]$	2c[b]

[a] This potential was given as −0.5 V vs SCE in ref 5. It was converted to the ferrocene reference potential in this table by addition of −0.45 V, as recommended in Table 3 of ref 2c. [b] Gross-Lannert, R.; Kaim, W.; Olbrich-Deussner, B. *Inorg. Chem.* **1990**, *29*, 5046.

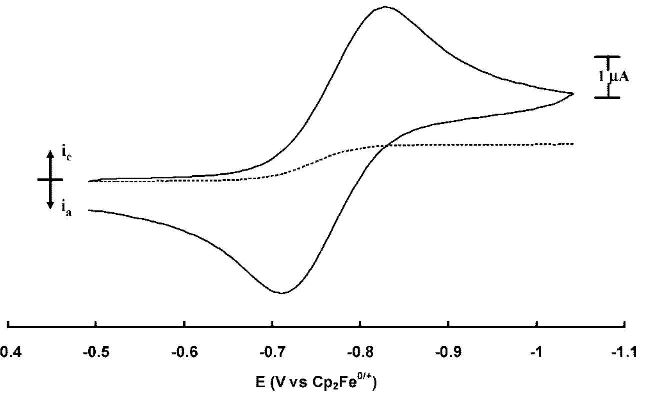

Figure 4. Voltammograms after exhaustive anodic electrolysis of 0.8 mM **1** in CH_2Cl_2/0.05 M $[NBu_4][B(C_6F_5)_4]$ at 268 K. Scan rates: CV (solid line), 200 mV/s; LSV (dashed line), 1 mV/s. The fact that the LSV currents are strictly cathodic shows that the analyte ($\mathbf{1}^+$) is exclusively in the oxidized form.

systems, although in these comparisons, the substitutions have all involved the formally charged (1,3,5) pentadienyl positions, rather than the uncharged (2,4) positions. One may, however, glean something about the effect of methylation at the uncharged positions by comparing the data for **1** with that reported for $Fe(C_6Me_6H)(C_6Me_6CH_2Ph)$ (Table 5). The addition of methyl groups to all four formally uncharged (2,4) positions can be seen to have led to a further stabilization of Fe(III), evidenced by the −170 mV change in potential, ca. −42 mV per CH_3 substitution. Although the difference (vs −53 mV) is relatively small, it would seem reasonable that a greater effect would be observed when substitution occurs directly on the atoms that would likely bear more charge. In fact, this trend is reminiscent of observations made for the C−O stretching frequencies of open and half-open vanadocene carbonyls, for which the back-bonding interaction with the CO ligand was also particularly enhanced by the presence of methyl substituents in the formally charged positions, rather than in the uncharged positions (i.e., 1,5 > 3 > 2,4).[18]

Interestingly, electrochemical data for analogues of Fe(6,6-dmch)$_2$, having the CMe_2 bridge replaced by $SiMe_2$ or $SnMe_2$ bridges, have been reported.[3j] Following the recommendation specified in footnote a of Table 5, their respective $E_{1/2}$ values would be ca. −0.28 and −0.65 V vs ferrocene. A clear explanation for the trends involving these species is not evident. In addition to substituent atom electronegativity, differences in C1--C5 separations could play a role, as could the angular deviations of the substituent atoms from the dienyl ligand planes. More data would clearly be needed in order to gain an understanding of the observed differences, and perhaps an examination of $GeMe_2$-bridged complexes would be especially useful.

Spectral Characterization of $\mathbf{2}^+$and $\mathbf{3}^+$. Both ESR and optical spectroscopy were used to characterize the 17 e^- cations $\mathbf{2}^+$ and $\mathbf{3}^+$ produced through bulk electrolysis. ESR spectroscopy has been shown to be particularly effective for the characterization of d^5 systems of this type.[19] Whereas ferrocenium and many of its derivatives are subject to fast relaxation effects, which may require very low temperature conditions, pseudosandwich Fe(III) complexes of lower symmetry do not suffer from this requirement, and frozen spectra were easily observed at 77 K for the radical cations $\mathbf{2}^+$ and $\mathbf{3}^+$. The clean rhombic spectra had *g*-values of 2.191, 2.105, and 2.013 for $\mathbf{2}^+$ and 2.192, 2.097, and 2.023 for $\mathbf{3}^+$, being similar to values reported for other open ferroceniums.[3e,20] As discussed in detail elsewhere,[19,20] analysis of the directional *g*-values is helpful in assigning the electronic structure of Fe(III) sandwich and pseudosandwich complexes. In the present case, the fact that the *g*-values are all above 2.0 with a spread of only 0.17 to 0.18 units is consistent with the SOMOs of $\mathbf{2}^+$ and $\mathbf{3}^+$ having their major components be the iron d_{z^2} orbital.

Visible absorption spectra were obtained for $\mathbf{2}^+$ and $\mathbf{3}^+$ from solutions generated in the bulk electrolysis experiments. Both of the cations displayed a band of modest intensity, likely originating from ligand-to-metal charge transfer, at a fairly low energy, with $\lambda_{max} = 768$ nm for $\mathbf{2}^+$ and 758 nm for $\mathbf{3}^+$. Assuming quantitative electrolytic conversion of the neutral compounds to the cations, the extinction coefficients were approximately 760 M^{-1} cm^{-1} (optical spectra are available in Figure 5 and in the Supporting Information).

Reactions of 1–3 with TCNE. The very mild redox potentials of the iron systems suggested that they might be readily oxidized by mild oxidizing agents. Indeed, addition of a benzene solution of the neutral iron complex to an equimolar quantity of TCNE in the same solvent gave an immediate color change to light yellow-orange with formation of a darker solid. Workup gave 60–68% yields of analytically pure 1:1 salts of the Fe(cyclohexadienyl)$_2$ cations with the $[TCNE]^-$ ion. Although there is considerable precedence[21−23] for equilibration of metallocene/TCNE radical ion pairs with neutral donor/acceptor pairs (eq 2), we found no evidence of this in the present case.

$$\text{Donor} + \text{Acceptor}^- \rightleftharpoons \text{Donor}^+ + \text{Acceptor} \tag{2}$$

This is consistent with the fact that the $E_{1/2}$ value for the reduction of TCNE to the corresponding anion is positive of those of the oxidations of the iron complexes by over 200 mV, providing a strong thermodynamic driving force for the formation of radical ion pairs in these systems. In contrast to the slight

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(18) (a) Newbound, T. D.; Rheingold, A. L.; Ernst, R. D. *Organometallics* **1992**, *11*, 1693. (b) Gedridge, R. W.; Hutchinson, J. P.; Rheingold, A. L.; Ernst, R. D. *Organometallics* **1993**, *12*, 1553.

(19) Rieger, P. H. *Coord. Chem. Rev.* **1994**, *135*, 203.

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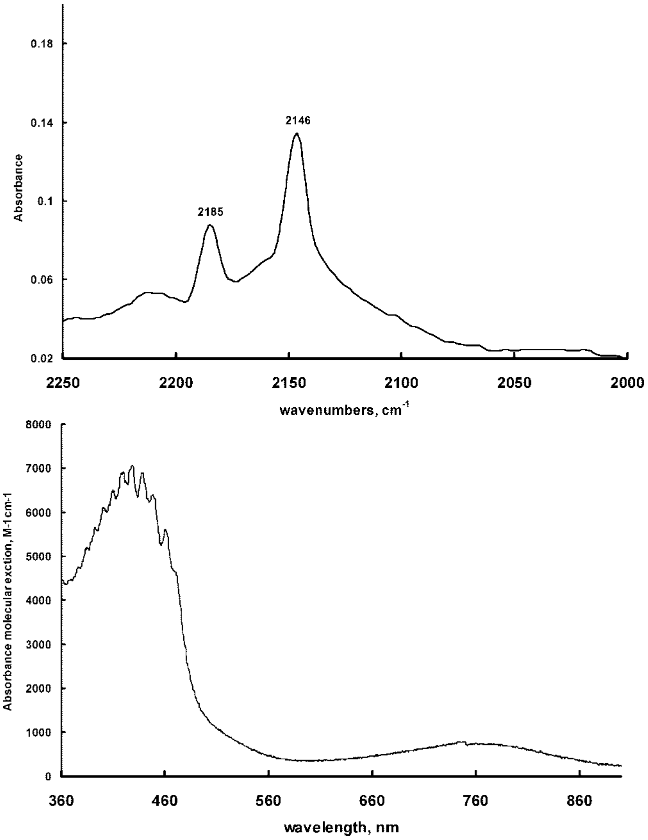

Figure 5. Spectra of [**2**][TCNE]. Top: IR in Nujol mull. Bottom: optical in CH_2Cl_2.

structural changes accompanying oxidation of ferrocene, the oxidation of the open ferrocenes should be accompanied by significant conformational changes,[3e] which would make structural assessments of the solid state natures of their TCNE salts much easier.

The IR and optical spectra of [**2**][TCNE] are consistent with observations made for this group of 1:1 salts. A Nujol mull IR spectrum (Figure 5, top) shows bands at 2185 and 2146 cm^{-1}, which are assigned to the nitrile stretches of the $[TCNE]^-$ ion.[20–22] The optical spectrum in CH_2Cl_2 (Figure 5, bottom) displayed two absorptions, each consistent with 1 equiv of the expected ion. The absorption at $\lambda_{max} = 768$ nm is attributed to $\mathbf{2}^+$, while the strong band with fine structure at λ_{max} 434 nm is assigned to the well-characterized absorption of the TCNE anion.[24] The apparent extinction coefficient for the TCNE anion band calculated from these experiments is 7.06×10^3 M^{-1} cm^{-1}, in excellent agreement with the literature value[24] of 7.10 $\times$ 10^3 M^{-1} cm^{-1}, showing that virtually all of the [**2**][TCNE] salt is present as a pair of radical ions in solution. Similar findings were made for [**3**][TCNE] in CH_2Cl_2, although the measured apparent extinction coefficient for $[TCNE]^-$ was slightly lower, namely, 6.74×10^3 M^{-1} cm^{-1}. Less definitive results were obtained on the Nujol mull IR spectra of [**3**][TCNE].[25]

Conclusions

This work has shown that one-electron oxidations of pseudoferrocenes that are substituted at the formally charged 1, 3, and/or 5 positions of the cyclohexadienyl ring by methyl or by SiR_3 (R = Me or *i*-Pr) groups give 17-electron cations that are persistent on the electrolytic and synthetic time scales, in contrast to their less stable nonbridged (open ferrocene) analogues.[20] Befitting the facile redox potentials of these compounds (in the range of -0.5 to -0.8 vs ferrocene), some members of this family are even easier to oxidize than decamethylferrocene. The 18-electron compounds readily undergo one-electron transfer reactions with mild to weak oxidizing agents such as TCNE in a 1:1 stoichiometry, which further amplifies the model of bis(cyclohexadienyl)iron complexes as ferrocene mimics.

Acknowledgment. We thank the National Science Foundation (CHE 04-11703), the University of Utah, and the Petroleum Research Fund for support of this research.

Supporting Information Available: Optical spectrum of $\mathbf{3}^+$ and an ESR spectrum of $\mathbf{3}^+$ in CH_2Cl_2 at 77 K. CIF files for each of the crystal structures. This material is available free of charge via the Internet at http://pubs.acs.org.

OM700886K

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(24) Frey, J. E.; Du Pont, L. E.; Puckett, J. J. *J. Org. Chem.* **1994**, *59*, 5386.

(25) A weak absorbance at 2213 cm^{-1} found in this spectrum is assigned to neutral TCNE.