Investigation of the Role of Silicon and Its Nonplanar Tetrahedral Coordination in the Transmission of Charge in a Mixed-Valent Binuclear Iron Complex: Synthesis and Characterization of a $TCNE^{\bullet-}$ Salt of $Cp^*Fe(\mu\text{-}C_{14}H_{18}Si_2)FeCp^*$

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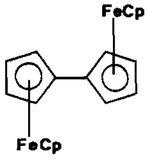
Introduction

Mixed-valent, binuclear iron π-complexes bridged by biferrocenyl (I) and fused polyaromatic hydrocarbon ligands (II) have been extensively studied from the perspective of valence detrapping.[1,2] One manifestation of charge delocalization in binuclear iron(II) compounds is the observation of a large separation (∼1 V) between the first and second oxidation potentials in the cyclic voltamogram of π-delocalized compounds such as $(Cp^*Fe)_2(\mu\text{-}s\text{-indacene})$, II. Valence detrapping in $[(Cp^*Fe)_2(\mu\text{-}s\text{-indacene})^+][BF_4^-]$, II^+, has been investigated by Mossbauer spectroscopy.[3] The results of electrochemical, Mossbauer, and other spectroscopic studies have been shown to be consistent with complete detrapping in II over the range 1.5–300 K.[2–4] The recently reported bis(η^5-1,2,3,4,5-pentamethyl-2,4-cyclopentadien-1-yl)[*trans*-μ-{(1)9–12-η:3–7-η}-2,2,8,8-tetramethyl-2,8-disilatricyclo[7.3.0.$0^{3,7}$]dodeca-3,5,9,11-tetraene-1,7-diyl]diiron(II), III, provides an opportunity for investigation of (1) the effect of silicon on the valence detrapping between two iron centers through *σ-conjugation* and (2) the effect of changing the structure of the bridging ligand from a nearly planar to a distinctly bent conformation owing to the approximate tetrahedral geometry about the bridging silicon atoms.[5] Polysilanes, $-(SiR_2)_n-$, are reported to mimic the properties of polyconjugated hydrocarbons.[6] Extensive delocalization of charge in these exclusively *σ-conjugated* polymers has been suggested by others on the basis of ionization potential, electron affinity, absorption spectra, ESR spectra, and photoconductivity measurements.[6] In the present note, we describe the synthesis and characterization of a $TCNE^{\bullet-}$ salt of III.



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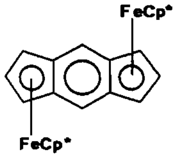

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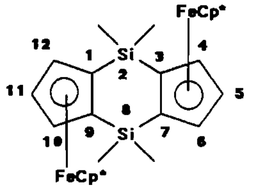
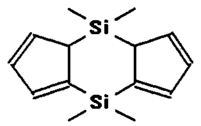


III

Experimental Section

All compounds described in this work were handled using Schlenk techniques, an M. I. Braun glovebox under a purified argon atmosphere, or a vacuum line equipped with oil diffusion and mechanical pumps.[7] Anhydrous $FeCl_2$ was purchased from Strem Chemical Co. and used as received. A solution of 1.6 M ^nBuLi in hexanes was purchased from Aldrich Chemical Co. Tetracyanoethylene (TCNE) was purchased from Aldrich Chemical Co. and sublimed prior to use. Solvents were purified by refluxing over Na/benzophenone (toluene, tetrahydrofuran, diethyl ether, pentane, hexane) or P_2O_5 (dichloromethane) and distilled prior to use. C_6D_6 was purchased from Cambridge Isotope Laboratories and dried over Na/benzophenone as described above. The μ-bridging ligand IV (Cp*H, 2,2,8,8-tetramethyl-2,8-disilatricyclo[7.3.0.$0^{3,7}$]dodeca-3,5,9,11-tetraene) and the corresponding iron complex III (bis(η^5-1,2,3,4,5-pentamethyl-2,4-cyclopentadien-1-yl)[*trans*-μ-{(1)9–12-η:3–7-η}-2,2,8,8-tetramethyl-2,8-disilatricyclo[7.3.0.$0^{3,7}$]dodeca-3,5,9,11-tetraene-1,7-diyl]diiron(II)) were prepared by a literature method.[5]



IV

^1H spectra were recorded on a Varian 300XL spectrometer in 5-mm tubes equipped with a Teflon valve (Wilmad Glass Co.). Proton chemical shifts are listed relative to residual protons in the solvent (C_6D_5*H* at δ 7.15 ppm). Elemental analyses (C, H, N) were performed by Galbraith Laboratories, Inc. Variable-temperature Mossbauer spectra were recorded on a standard constant-acceleration apparatus and fit to standard independent Lorentzians using a locally modified version of the program as discussed by Bancroft.[8] Cyclic voltammetry was performed in a BAS 100B electrochemical analyzer.

Synthesis of III. While the synthesis of III was performed according to literature procedures, we obtained a better resolved ^1H NMR spectrum. ^1H (C_6D_6): δ 0.592 (s, 12H, Si*Me*$_2$), 1.733 (s, 30H, *Cp**), 3.860 (d, 4 H, *J* = 2.1 Hz, H(4), H(6), H(10), H(12)), 3.947 (t, 2 H, *J* = 2.1 Hz, H(5), H(11)). The Mossbauer spectrum of III at 293 K consisted of a doublet centered at 0.43 mm/s with quadrupole splitting ΔE = 2.41 mm/s. These parameters are typical of "ferrocene-like" iron and confirm the essential purity of the dimer product vis-a-vis iron species.[9]

Reaction of II with TCNE: Preparation of $[(Cp^*Fe)_2(\mu\text{-}C_{14}H_{18}Si_2)^+][TCNE^{\bullet-}]$, V. A 20.5-mg sample (0.16 mmol) of TCNE was dissolved in 10 mL of diethyl ether, and the mixture was added dropwise to a solution of 100 mg (0.16 mmol) of II in 10 mL of pentane with vigorous stirring at ambient temperature. A black precipitate formed immediately. A 117-mg amount (97% yield) of $[(Cp^*Fe)_2(\mu\text{-}C_{14}H_{18}Si_2)^+][TCNE^{\bullet-}]$, V, was isolated as described above. Anal. Calcd for $C_{40}H_{48}Si_2FeN_4$: C, 63.83; H, 6.43; N, 7.44. Found: C, 62.55; H, 6.46; N, 7.48.

Cyclic Voltammetry Studies of III. A dichloromethane solution 2 mM in III, 2 mM in Cp^*_2Fe (as a reference), and 0.1 M in $(^nBu_4N)ClO_4$ was prepared under nitrogen in a electrochemical cell fitted with a gold working electrode, a silver wire reference electrode, and a platinum wire as an auxiliary electrode. The sample was scanned at a rate of 100 mV/s over a range −800 to +300 mV. Three reversible oxidations were observed at +0.328, +0.06, and −0.12 V. The latter potential corresponds to the oxidation of Cp^*_2Fe. All potentials are reported relative to SCE.

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(1) (a) Morrison, W. H., Jr.; Hendrickson, D. N. *J. Chem. Phys.* **1973,** *59,* 380. (b) Morrison, W. H., Jr.; Hendrickson, D. N. *Inorg. Chem.* **1975,** *15,* 2331. (c) Webb, R. J.; Geib, S. J.; Staley, D. L.; Rheingold, A. L.; Hendrickson, D. N. *J. Am. Chem. Soc.* **1990,** *112,* 5031 and references therein.

(2) (a) Reiff, W. M.; Manriquez, J. M.; Ward, M. D.; Miller, J. S. *Mol. Cryst. Liq. Cryst.* **1989,** *176,* 423. (b) Iijima, S.; Saida, R.; Motoyama, I.; Sano, H. *Chem. Soc. Jpn.* **1981,** *54,* 1375.

(3) Reiff, W. M.; Manriquez, J. M.; Miller, J. S. *Hyperfine Inter.* **1990,** *53,* 397.

(4) Manriquez, J. M.; Ward, M. D.; Reiff, W. M.; Calabrese, J. C.; Jones, N. L.; Carroll, P. J.; Bunel, E. E.; Miller, J. S. *J. Am. Chem. Soc.,* in press.

(5) Siemelling, U.; Jutzi, P.; Neumann, B.; Stammler, H.-G. *Organometallics* **1992,** *11,* 1328.

(6) (a) Miller, R. D.; Michl, J. *Chem. Rev.* **1989,** *89,* 1410. (b) West, R. Organopolysilanes. In *Comprehensive Organometallic Chemistry*; Wilkinson, G., Stone, F. G. A., Abel, E. W., Eds.; Pergamon Press: New York, 1982; Vol. 1, p 365.

(7) Shriver, D. F. *Manipulation of Air Sensitive Compounds*; McGraw-Hill: New York, 1969.

(8) (a) Cheng, C.; Reiff, W. M. *Inorg. Chem.* **1977,** *16,* 2092. (b) Bancroft, G. M.; Maddock, A. G.; Ong, W. K.; Prince, R. H.; Stone, A. J. *J. Chem. Soc. A* **1967,** 1966.

(9) Greenwood, N. N.; Gibb, T. C. *Mossbauer Spectroscopy*; Chapman and Hall, Ltd.: London, U.K., 1971.

0020-1669/94/1333-1562$04.50/0

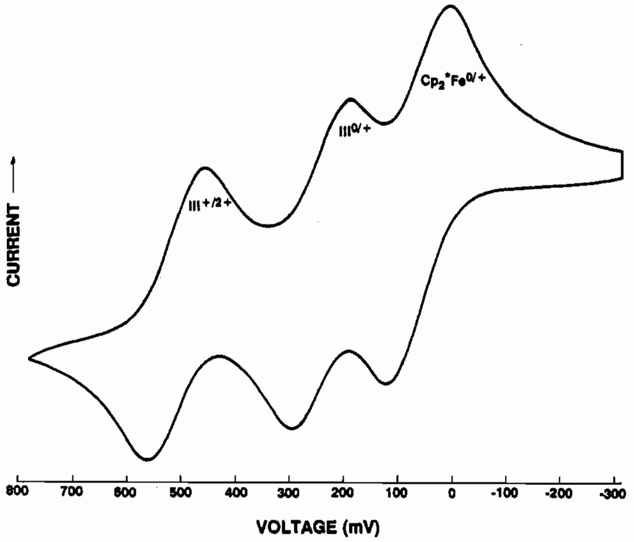

Figure 1. Cyclic voltamogram of **II** (2.0 mM), $Cp^{*}{}_2Fe$ (2.0 mM as a reference), and $(^{n}Bu_4N)ClO_4$ (0.1 M) in CH_2Cl_2.

Table 1. Difference of Oxidation Potentials (ΔE) in Selected Binuclear Iron Complexes

complex	*n*	ΔE (V)
$CpFe(\mu\text{-}C_5H_4(CH_2)_nC_5H_4)FeCp$	2	0.00
	1	0.10
$CpFe(\mu\text{-}C_5H_4(SiMe_2)_nC_5H_4)FeCp$	3	0.08
	2	0.11
	1	0.15
III		0.27
I		0.34
II		0.82

Results and Discussion

Electrochemical oxidation of **III** in CH_2Cl_2 shows two reversible oxidations at +0.328 and +0.06 V relative to SCE (Figure 1). The separation between the two oxidation waves, $\Delta E = 0.268$ V, is considerably less than the 0.82-V separation observed in the fused π-conjugated (μ-symmetric indacene) iron dimer **II**. If the magnitude of ΔE is a measure of transmission of charge between ferrocene-like units,[10] then, by comparison with **I**,[10] saturated hydrocarbon-bridged diferrocenes,[11] and α,ω-bis(ferrocenyl)-oligosilanes[10] (Table 1), compound **III** is similar to **I** in its effectiveness at delocalizing charge but considerably poorer than **II**.

Compound **III** reacted with tetracyanoethylene (TCNE) in nearly quantitative yield to form $[(Cp^{*}Fe)_2(\mu\text{-}C_{14}H_{18}Si_2)^{+}][TCNE^{\bullet-}]$, **V**. The ambient-temperature and 77 K ^{57}Fe Mossbauer spectra of **V** are shown in Figure 2 and are consistent with completely trapped low-spin Fe^{II} and low-spin Fe^{III} valence states. The 77 K spectrum (Figure 2b) is characterized by a doublet with isomer shift $\delta = 0.44$ mm/s (quadrupole splitting $\Delta E = 2.21$ mm/s) characteristic of the low-spin ferrocene-like Fe^{II} center and a doublet with $\delta = 0.46$ mm/s having a small $\Delta E = 0.26$ mm/s, typical of low-spin Fe^{III} (ferrocenium). The Mossbauer spectrum of the *s*-indacene system, $\mathbf{II}^{+}$, consists of a single doublet centered at 0.47 mm/s with a quadrupole splitting of 1.64 mm/s, intermediate between the typical values for ferrocene and ferrocenium and reflecting the complete detrapping and averaging of the valence states.[2,3] In this respect, the Mossbauer spectrum of **V** is similar to the reported spectrum of $[(Cp^{*}{}_2Fe)_2(\mu\text{-}as\text{-indacene})^{+}][BF_4^{-}]$.[2] The I_3^{-} salt of **III**, $[(Cp^{*}Fe)_2(\mu\text{-}C_{14}H_{18}Si_2)^{+}][I_3^{-}]$, was also prepared to test for any anion dependence of the valence detrapping behavior. As shown in Figure 3, the Mossbauer spectrum for $[(Cp^{*}Fe)_2(\mu\text{-}C_{14}H_{18}Si_2)^{+}][I_3^{-}]$ is similar to that of **V** at ambient temperature save for the fact that quadrupole splitting of the low-spin Fe^{III} is less resolved and again consistent with a valence-trapped mixed-valent iron compound. For the I_3^{-} system, the apparent difference in intensities between the outer (low-spin Fe^{II}) doublet and inner (low-spin Fe^{III}) absorption is the result of a difference in the temperature dependence of recoil-free fractions for these sites. Nevertheless, and as expected, at 4.6 K, $I_{Fe(II)}/I_{Fe(III)} \approx 1.0$. The widths of the resolved spectral transitions are farily typical for the medium thickness samples of the type under consideration, i.e. ≈0.30–0.35 mm/s, and are not remarkable.

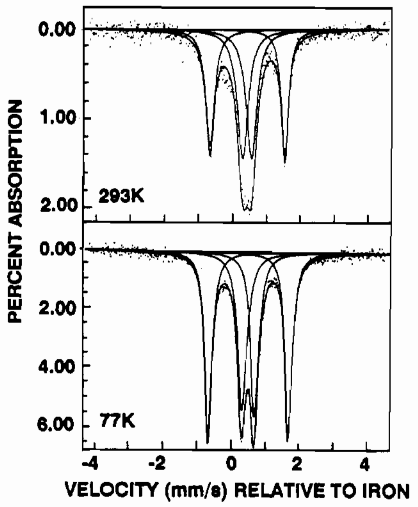

Figure 2. ^{57}Fe Mossbauer spectra of **V** at (a) 293 K and (b) 77 K.

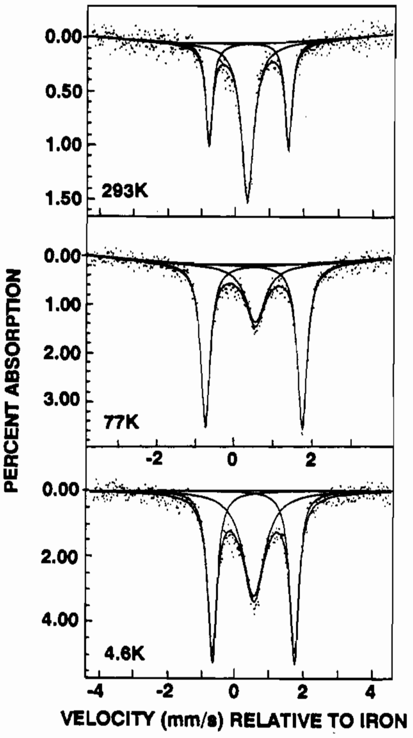

Figure 3. ^{57}Fe Mossbauer spectra of $[(Cp^{*}Fe)_2(\mu\text{-}C_{14}H_{18}Si_2)^{+}][I_3^{-}]$ at (a) 293 K, (b) 77 K, and (c) 4.6 K.

On heating of compound **V** to 388 K, the spectrum changed considerably compared to that obtained at ambient temperature, such that the inner transitions became more intense relative to the outer ones. However, no clear indication of detrapping is observed at this temperature. Further increases in the temperature to 512 K leads to complete disappearance of the spectrum. Upon cooling of the sample, a quadrupole doublet characteristic of Fe^{II}

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[10] Dement'ev, V. V.; Cervantes-Lee, F.; Parkyanyi, L.; Sharma, H.; Pannell, K. H.; Nguyen, M. T.; Diaz, A. *Organometallics* **1993**, *12*, 1983.

[11] Morrison, W. H., Jr.; Krogsrud, S.; Hendrickson, D. N. *Inorg. Chem.* **1973**, *12*, 1998.

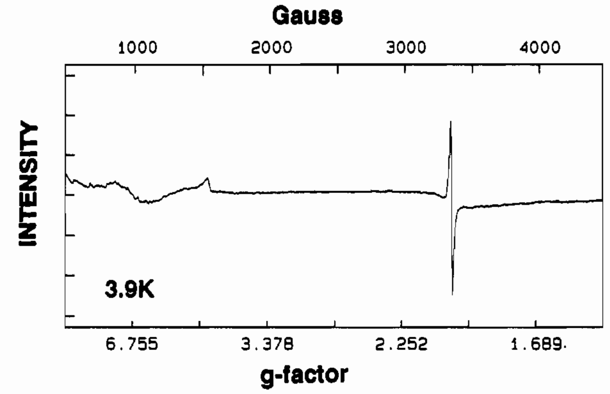

Figure 4. Solid-state X-band ESR spectra of V at 3.9 K.

centered at 0.42 mm/s with quadrupole splitting = 2.37 mm/s (characteristic of ferrocene) was observed. In an independent experiment, thermolysis of V at 512 K led to decomposition of the compound. Small quantities of the mixed-ligand ferrocene Cp*FeCp could be sublimed from the residue and were identified by ^{1}H NMR.

In comparison with characterized [(Cp*Fe)$_2$(μ-*s*-indacene)], II, the observation of two, single-electron oxidations in III is consistent with some degree of interaction between the two iron centers in III on the electrochemical time scale ($\sim 10^{-1}$ s^{-1}). On the Mossbauer time scale ($\sim 10^7$ s^{-1}), however, $[(Cp^*Fe)_2(\mu\text{-}C_{14}H_{18}Si_2)^+][TCNE^{\bullet -}]$, V, and its I_3^- analogue are apparently completely valence trapped. It remains an open question, however, as to whether the observed behavior reflects less facile transmission of charge through the silicon atoms of the bridging ligand or is predominantly the effect of a difference in structure from the completely detrapped, essentially planar π-fused ring systems such as II and coupled biferrocenyl systems, I. On the basis of an observable X-band ESR resonance for TCNE$^{\bullet -}$ at $g \sim 2$ at 293 and 4.2 K in V (Figure 4), a "mixed stack" structure (Figure 5) typical for ferrocene-like polycyanide donor–acceptor systems is a likely choice.[12] An alternate structure possibility for V is a

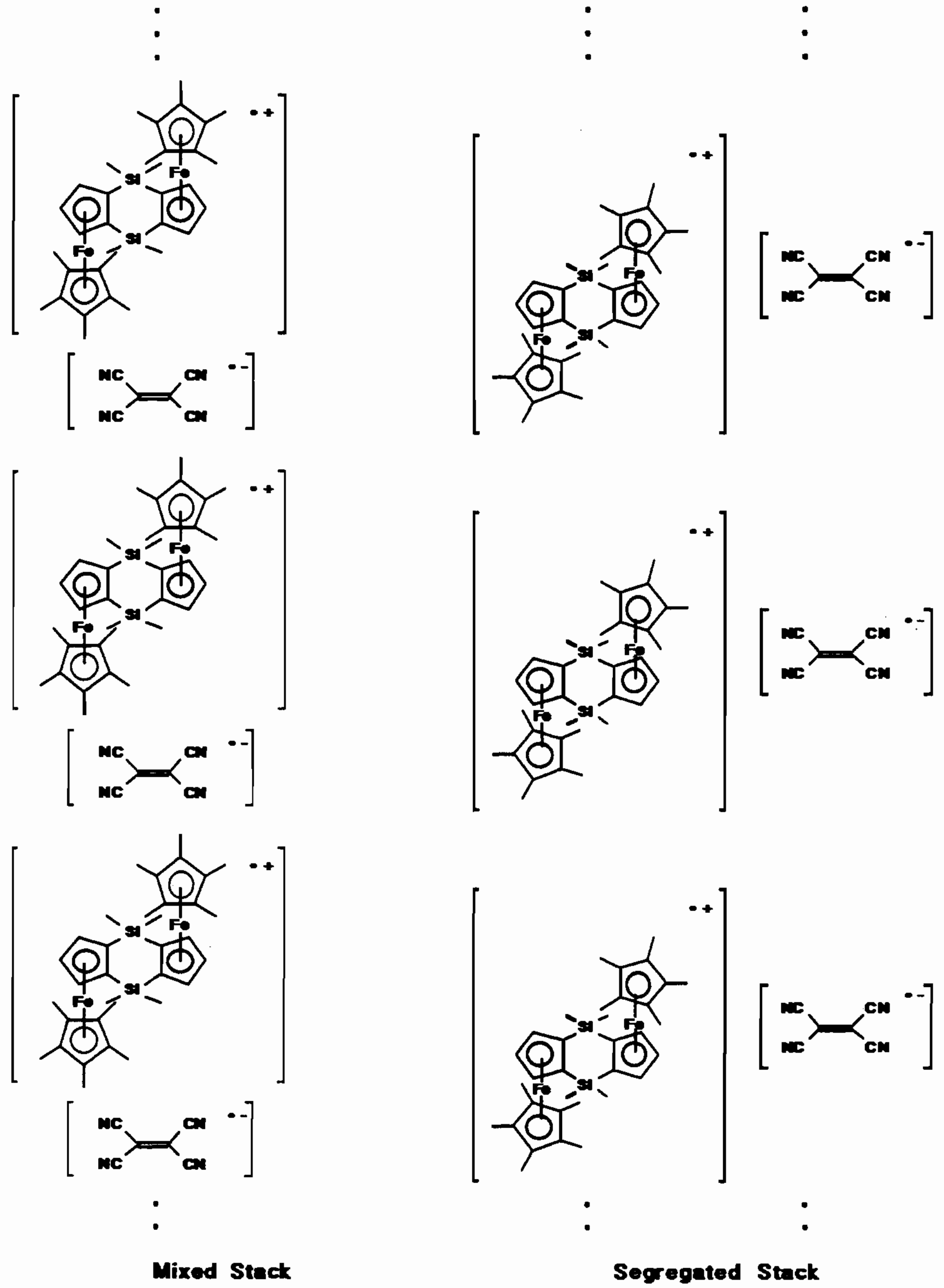

Figure 5. Possible structures for compound V.

segregated stack structure (Figure 5). This possibility, however, is less common for ferrocene-like polycyanide donor–acceptor systems. The segregated stack structure is further rejected in that it should show no ESR contribution from the $TCNE^{\bullet -}$ radical ions ($g \sim 2$), owing to strong antiferromagnetic coupling along its segregated chain. As seen in Figure 4, this signal is clearly evident.

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(12) (a) Miller, J. S.; Epstein, A. J.; Reiff, W. M. *Chem. Rev.* **1988**, *88*, 201. (b) Miller, J. S.; Epstein, A. J.; Reiff, W. M. *Acc. Chem. Res.* **1988**, *21*, 114.