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Structural and pH Control on the Electronic Communication between Two Identical Ferrocene Sites

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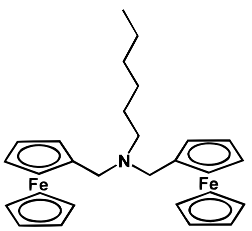
Summary: The preparation of a new type of dinuclear ferrocene compound containing a $-CH_2-N(R)-CH_2-$ *bridge is reported. These new dinuclear ferrocenes exhibit a moderate degree of electronic communication between the two ferrocene subunits, which is disrupted by protonation or N-methylation of the bridge's tertiary nitrogen atom.*

The extent of electronic intramolecular communication between two or more identical redox centers has received considerable attention. In this regard, compounds containing multiple ferrocene residues have been investigated extensively because of their synthetic accessibility and reversible voltammetric behavior.[1] In this communication we describe the preparation of a new type of dinuclear ferrocene compound in which a $-CH_2-N(R)-CH_2-$ bridge (or its positively charged, N-methylated analog) is used to connect two identical ferrocene subunits. Voltammetric data show conclusively that the extent of electronic communication between the two ferrocenes changes considerably upon N-methylation or protonation of the tether's tertiary amine nitrogen. These results provide a clear and novel example of pH and/or structural control on the degree of electronic interaction exhibited by two equivalent redox centers.[2]

Compound **1** was easily made in 60% yield by refluxing hexylamine with excess (ferrocenylmethyl)trimethylammonium iodide in CH_3CN for 3 h. Methylation of **1** with iodomethane followed by counterion exchange yielded the hexafluorophosphate salt of **1^+-Me**. Finally, the chloride salt of **2^+** was prepared (55% yield) by refluxing (ferrocenylmethyl)trimethylammonium iodide and ((dimethylamino)methyl)ferrocene in CH_3CN for 12 h followed by counterion exchange. All these reactions take advantage of the easy thermally induced dissociation of the (ferrocenylmethyl)trimethylammonium cation into the ferrocenylmethyl carbocation and trimethylamine in polar media.[3] All ferrocene dimers were fully characterized by ^1H and ^{13}C NMR spectroscopy, FAB MS, and elemental analysis (see the Supporting Information).



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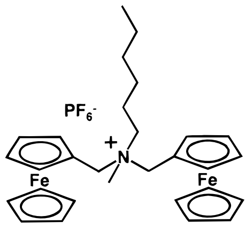
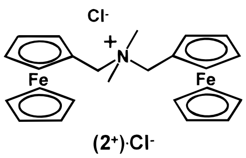


$(1^+$-Me)$\cdot PF_6^-$



$(2^+)\cdot Cl^-$

The electrochemical behavior of these ferrocene dimers was investigated in CH_3CN also containing 0.2 M tetrabutylammonium hexafluorophosphate (TBAHP) as the supporting electrolyte. Relevant electrochemical parameters obtained from these experiments are given in Table 1. The voltammetric behavior of the free amine (compound **1**) reveals two redox couples (Figure 1A). The corresponding half-wave potentials ($E_{1/2}$) are rather close, so that the two voltammetric waves, albeit clearly noticeable, are not fully resolved. The experimental voltammogram was fitted to digitally simulated voltammograms.[4] From the optimization of this fitting analysis, we determined values of 0.420 and 0.502 V vs Ag/AgCl for the two consecutive oxidation potentials. The corresponding $\Delta E_{1/2}$ value of 82 mV reveals a modest level of electronic communication between the two ferrocene residues.[5] The corresponding equilibrium constant (K_c) for the comproportionation reaction ($Fc-Fc + Fc^+-Fc^+ = 2Fc^+-Fc$) was 24. Addition of HCl to this solution results in the anticipated protonation of the tertiary nitrogen, as evidenced by the ^1H NMR spectra shown in Figure 2. The protonated form of this ferrocene dimer (**1^+-H**) exhibits a voltammetric behavior (Figure 1B) that reveals a diminished extent of electronic communication. The two redox waves are now completely unresolved, and fitting of the experimental voltammogram to digital simulations yields values of 0.601 and 0.647 V for the corresponding $E_{1/2}$ values. Both half-wave potentials are shifted in the anodic direction, reflecting the increased electron-withdrawing nature of the bridging tether upon protonation. However, the key finding is that the difference between the two oxidation potentials ($\Delta E_{1/2}$) shrinks to 46 mV (K_c = 6.1), indicating that the level of electronic communica-

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(1) For a recent review, see: Barlow, S.; O'Hare, D. *Chem. Rev.* **1997**, *97*, 637.

(2) For biochemical examples of similar phenomena, see, for instance: (a) Moltke, S.; Krebs, M. P.; Mollaaghababa, R.; Khorana, H. G.; Heyn, M. P. *Biophys. J.* **1995**, *69*, 2074. (b) Bobrowski, K.; Holcman, J.; Poznanski, J.; Wierzchowski, K. L. *Biophys. Chem.* **1997**, *63*, 153.

(3) (a) Marr, G.; Rockett, B. W.; Rushworth, A. *Tetrahedron Lett.* **1970**, *16*, 1317. (b) Pennie, J. T.; Bieber, T. I. *Tetrahedron Lett.* **1972**, *34*, 3535.

(4) We used the commercially available software package DigiSim (Bioanalytical Systems, West Lafayette, IN).

(5) Flannagan, J. B.; Margel, S.; Bard, A. J.; Anson, F. C. *J. Am. Chem. Soc.* **1978**, *100*, 4248.

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Table 1. Electrochemical Parameters for the Oxidation of Dinuclear Ferrocenes Measured at 25 °C in 0.2 M TBAHP/CH$_3$CN Solution[a]

	1	**1$^+$-H**	**1$^+$-Me**	**2$^+$**
$E_{p,a}$ (V vs ferrocene)	0.059	0.201	0.296	0.282
$E_{p,c}$ (V vs ferrocene)	−0.048	0.135	0.222	0.201
$i_{p,a}$ (μA)	2.13	2.28	1.78	2.61
$i_{p,c}$ (μA)	1.84	2.23	1.57	2.43
$i_{p,a}/i_{p,c}$	1.1	1.02	1.14	1.07
ΔE_p (mV)	107	66	74	81
$(E_{1/2})^1$ (V vs ferrocene)	−0.008	0.173	0.213	0.207
$(E_{1/2})^2$ (V vs ferrocene)	0.074	0.219	0.271	0.264
$\Delta E_{1/2}$ (mV)	82	46	58	57
K_c	24	6.1	9.6	9.1

[a] $E_{p,a}$ and $E_{p,c}$ are the anodic and cathodic peak potentials, $i_{p,a}$ and $i_{p,c}$ are the peak currents, ΔE_p stands for the peak-to-peak potential splitting $|E_{p,a} - E_{p,c}|$, $(E_{1/2})^1$ and $(E_{1/2})^2$ are the half-wave potentials for the two successive one-electron oxidations of these dinuclear ferrocenes, $\Delta E_{1/2}$ represents the difference between the two half-wave potentials, and K_c is the comproportionation constant (see text for a definition).

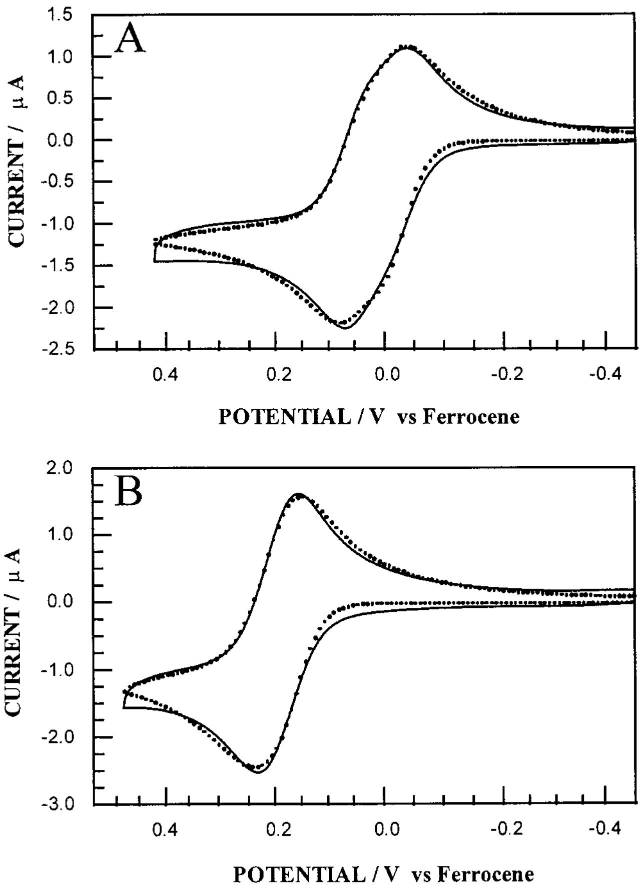

Figure 1. Cyclic voltammetric response on a glassy-carbon electrode of a 0.2 mM solution of **1** in 0.2 M TBAHP/CH$_3$CN (A) before and (B) after protonation with aqueous HCl. Dotted traces correspond to best-fit simulated voltammograms obtained with DigiSim using the parameters listed in Table 1.

tion between the ferrocenes observed in the free amine is lost upon protonation. This phenomenon is fully reversible, and the voltammetric behavior of Figure 1A can be recovered by neutralization with NaOH of the HCl previously added to the solution. We also surveyed the voltammetric behavior of the fully quaternized compounds **1$^+$-Me** and **2$^+$**. These *N*-methylated dinuclear ferrocenes show $E_{1/2}$ values similar to those measured with protonated **1$^+$-H**, again reflecting that the generation of positive charge on the bridge's nitrogen leads to the relative destabilization of the oxidized forms of these compounds. The $\Delta E_{1/2}$ and K_c values for the N-methylated dinuclear ferrocene compounds are also much closer to those of **1$^+$-H** than to those measured for **1**. Therefore, N-methylation and protonation have a similar deleterious effect on the communication between the two ferrocene subunits. A feasible explanation is that the positive charge on the nitrogen favors association with a counterion, which could help shield the two ferrocenes from one another, easing the independent development of positive charge in both redox centers. Attenuation of the polarizability of the spacer upon protonation or methylation of the nitrogen atom may also play a role.

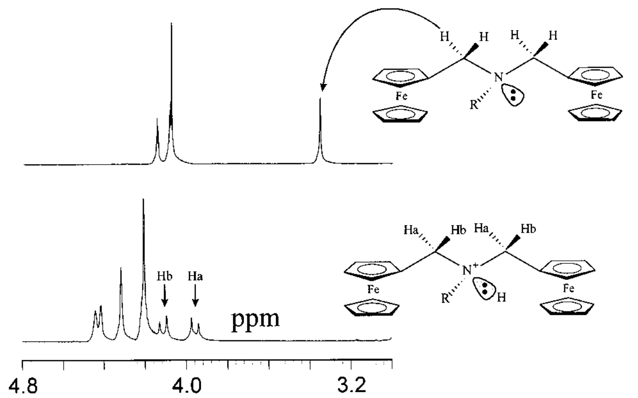

Figure 2. ^{1}H NMR spectra (400 MHz, CD$_3$CN) of dimer **1** before (top) and after treatment (below) with a 10-fold excess of DCl.

In summary, we have prepared a new class of dinuclear ferrocenes that contain a tertiary amine in the connecting tether. Our voltammetric data clearly show that the electronic interaction between the two identical redox centers is severely disrupted by the reversible (protonation) or irreversible (N-methylation) development of positive charge on the central nitrogen.

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Supporting Information Available: Text giving full details on the preparation of **1**, **1$^+$-Me**, and **2$^+$** and figures giving cyclic voltammetric data for **1$^+$-Me** and **2$^+$** and square-wave voltammetric data for **1** and **1$^+$-H**. This material is available free of charge via the Internet at http://pubs.acs.org.

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