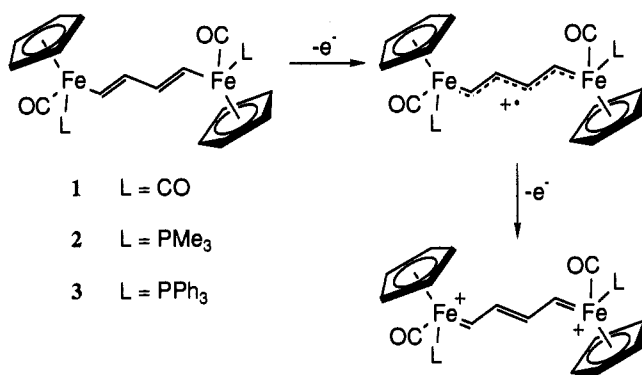# Mixed-Valence Diiron Complexes with Butadienediyl Bridges

Beth A. Etzenhouser, Marisa DiBiase Cavanaugh, Heather N. Spurgeon, and Michael B. Sponsler*

Department of Chemistry and W. M. Keck Center for Molecular Electronics Syracuse University, Syracuse, New York 13244-4100

Received August 16, 1993

Polyene segments are widely recognized for their ability to allow long-distance electronic coupling through π delocalization.[1-3] However, no transition-metal mixed-valence complexes[4-7] with polyenediyl bridges have yet been reported.[8] Herein we report the characterization of delocalized (class III) mixed-valence Fe^{II}/Fe^{III} complexes with butadienediyl bridges, prepared by one-electron oxidation of the corresponding Fe^{II}/Fe^{II} complexes $[CpFe(CO)(L)]_2(\mu\text{-CH}=\text{HCH}=\text{H})$ (1, L = CO; 2, L = PMe$_3$; 3, L = PPh$_3$; Cp = η^5-C$_5$H$_5$). The Fe^{III}/Fe^{III} complexes 2^{2+} and 3^{2+} have been prepared as well.

1	L = CO
2	L = PMe$_3$
3	L = PPh$_3$

Phosphine complexes **2** and **3** were prepared by photochemical substitution of **1**, which was made by using a literature procedure.[13] Diastereomeric mixtures (*meso:dl* ≈ 1:1) were obtained for both **2** and **3**. We were unable to efficiently separate the isomers of

complex **2**,[14] so oxidation studies were performed on the mixture. The isomers of complex **3** were easily separated due to differences in solubility.[15] We have not yet assigned the identity of these isomers;[16,17] they are referred to as **3a** and **3b**, where **3a** has the lower solubility and higher melting point. Our oxidation studies focused on **3a** and, in particular, **3b**.

Highly colored radical cation and dication samples were prepared by treating dichloromethane or tetrahydrofuran solutions of **1-3** with ferrocenium hexafluorophosphate (FcPF$_6$) at -78 °C.[20] For example, pale orange solutions (ca. 10⁻³ M) of the neutral complexes **3** gave dark brown solutions of the radical cations upon addition of a single equivalent of FcPF$_6$. Addition of a second equivalent gave dark purple solutions of the dications.

A single-line electron paramagnetic resonance (EPR) spectrum was obtained for **1**⁺ at -80 °C, but the signal was lost upon warming to -60 °C. The phosphine-substituted radical cations proved to be more stable, allowing spectra to be recorded at higher temperatures; the EPR signals for **3a**⁺ and **3b**⁺ decayed nonexponentially over about 1 h at -15 °C. These species exhibited hyperfine splitting that was strongly temperature dependent. At -86 °C, a broad, single-line spectrum was obtained for **3a**⁺, while **3b**⁺ gave a three-line spectrum (a_P = 7 G) at -82 °C. At -15 °C, the isomeric cations gave more complex patterns (Figure 1).

The EPR hyperfine patterns are consistent with mixed-valence species that are delocalized on the EPR time scale (about 10⁻⁸ s). A three-line pattern (a_P = 7.5 G) was obtained for **2**⁺ at -40 °C.[21] Simulations for **3a**⁺ and **3b**⁺ (Figure 1) were obtained by assuming that the unpaired electron is coupled to three pairs of $S = \frac{1}{2}$ nuclei, the phosphorus nuclei, and the protons on the bridging ligand.[22] An enormous reduction in the phosphorus coupling constant is observed with respect to the localized CpFe-(CO)(PPh$_3$)(CH$_3$)⁺ (a_P = 120 G),[24] even presuming that the largest coupling (8 or 7 G) is due to phosphorus. This probably indicates, in addition to delocalization over two metal centers, a

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(8) Related compounds include mixed valence dinuclear complexes with nitrogen-containing,[9] cumulenic,[10] or fulvalene[11] bridges and organometallic cyanines.[12]

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(14) ¹H NMR (C$_6$D$_6$): first isomer, δ 0.92 (d, 9.4, 18H), 4.17 (d, 1.4, 10H), 6.93 (m, 4H); second isomer, δ 0.93 (d, 9.4, 18H), 4.20 (d, 1.4, 10H), 6.85 (s, 4H). ¹³C NMR (C$_6$D$_6$): δ 19.2 (d, 29.6), 83.3, 136.3 (d, 37.5, first isomer), 135.9 (d, 37.5, second isomer), 151.2, 221.8 (d, 35.4, first isomer), 221.6 (d, 35.4, second isomer). IR (KBr): 1889, 1902 cm⁻¹. Anal. Calcd for C$_{22}$H$_{32}$Fe$_2$O$_2$P$_2$: C, 52.62; H, 6.42. Found: C, 52.47; H, 6.24.

(15) **3a**: mp 212 °C dec. ¹H NMR (C$_6$D$_6$): δ 4.20 (s, 10H), 6.67 (s, 4H), 7.00 (m, 18H), 7.60 (m, 12H). ¹³C NMR (CDCl$_3$) δ 84.7, 127.8 (d, 9.4), 129.3, 133.3 (d, 9.5), 136.8 (d, 41.3), 152.1, 221.9 (d, 33.0, low S/N); expected doublet near 133.6 was obscured. IR (KBr): 1911 cm⁻¹. Anal. Calcd for C$_{52}$H$_{44}$Fe$_2$O$_2$P$_2$: C, 71.42; H, 5.07. Found: C, 71.16; H, 5.22. **3b**: mp 180 °C. ¹H NMR (C$_6$D$_6$): δ 4.19 (s, 10H), 6.58 (m, 2H), 6.77 (m, 2H), 7.00 (m, 18H), 7.59 (m, 12H). ¹³C (CDCl$_3$): δ 84.8, 127.7 (d, 9.5), 129.2 (d, 1.4), 133.4 (d, 9.6), 133.6 (d, 14.2), 136.8 (d, 41.4), 152.1 (d, 2.4), 222.0 (d, 33.0). IR (KBr): 1915 cm⁻¹. Anal. Calcd for C$_{52}$H$_{44}$Fe$_2$O$_2$P$_2$: C, 71.42; H, 5.07. Found: C, 71.29; H, 4.91.

(16) Many potential methods to make this assignment have been tried without success, including X-ray crystallography, NMR chiral shift experiments, chromatography with chiral supports or solvents, stereoselective preparation, stereoselective conversion to less symmetrical products (Diels-Alder adducts, Fe(CO)$_3$ complexes), and degradative kinetic resolution. We are continuing to work on this problem.

(17) A very tentative assignment might be made by noting that the *meso* isomer can retain the crystallographic center of symmetry found in **1**.[18,19] Therefore, this isomer might be expected to have the lower solubility and higher melting point (i.e., **3a**), due to crystal packing effects.

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(20) Dication **1**²⁺ was not formed under these conditions, since its second oxidation potential is too high.

(21) Interpretation of this hyperfine pattern must be made with caution, given that the sample is an isomeric mixture.

(22) The presence of C-C rotamers of the radical cation species may account for our inability to more accurately simulate the spectra. Although electrochemical oxidation at low temperatures has been shown to induce isomerization of related iron alkenyl complexes,[23] no isomerization was detected after reduction of **3a**⁺ and **3b**⁺ to the neutral complexes, neither with respect to alkene stereochemistry nor configuration at iron. Nonetheless, rotamers about the central C-C bond in the radical cations are still possible.

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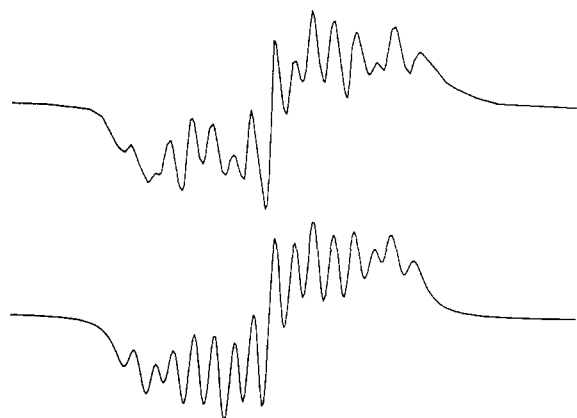(24) Therien, M. J.; Trogler, W. C. *J. Am. Chem. Soc.* **1987,** *109,* 5127-5133.

Figure 1. EPR spectrum (top) obtained at –15 °C for **3b⁺** (g = 2.024), along with a simulated spectrum (bottom) obtained by allowing coupling to three pairs of S = $^1/_2$ nuclei with hyperfine coupling constants of 7.0, 3.3, and 1.9 G.[31] A simulation for the spectrum of **3a⁺** (g = 2.022, not shown) gave coupling constants of 8.05, 3.3, and 1.9 G.

change in the character of the singly occupied molecular orbital at the metal centers for the dinuclear radical cations.

IR spectra obtained for **3b** and its oxidized forms at –40 °C in dichloromethane are also consistent with a delocalized structure for **3b⁺**. The presence of a single carbonyl stretching band for **3b⁺** at 1946 cm⁻¹, positioned approximately midway between the bands for **3b** and **3b²⁺** (1912 and 2012 cm⁻¹, respectively), indicates that the mixed valence-species is delocalized on the IR time scale (ca 10^{-12} s). Each band had a full width at half maximum of about 30 cm⁻¹, indicating that they were not significantly broadened by exchange. This experiment, more than any others described here, allows the classification of **3b⁺** as a class III mixed-valence complex.

In room temperature cyclic voltammetry (CV), complex **1** showed a chemically irreversible oxidation wave. However, at –78 °C, a quasireversible wave was obtained at $E°'$ = 0.06 V vs Fc⁰/⁺.[25] The phosphine derivatives each gave two reversible oxidation waves at room temperature and at –78 °C. The low-temperature $E°'$ values were –0.67 and –0.26 V for **2**, –0.54 and –0.12 V for **3a**, and -0.58 and –0.13 V for **3b**. The separation between these waves, from 410 to 450 mV, indicates a high degree of coupling between the metal centers. In related phenylene-bridged diiron complexes, this separation was 280 mV or less.[26]

Controlled potential electrolysis was performed on **3b** at –78 °C, in order to confirm that the product from the first CV oxidation was the same as the chemical oxidation product responsible for the EPR spectrum. After bulk oxidation of the sample to –0.4 V, the same two waves were again observed by CV, indicating that the oxidation product was stable on the time scale of the bulk oxidation (ca. 2 h). The EPR spectrum of this sample was identical to that shown in Figure 1. After controlled potential oxidation of **3b⁺** to **3b²⁺** (0.0 V), the CV results were again unchanged. This sample was EPR silent, except for a small residual **3b⁺** signal. Both oxidations were shown to involve a single electron per molecule by coulometry in the bulk oxidations.

A ¹H NMR spectrum obtained for the dication **3b²⁺** at –80 °C (CD₂Cl₂) showed resonances at 16.7 and 12.9 ppm for the bridge protons, supporting the proposed biscarbene structure. These values are appropriately shifted from those reported for CpFe(CO)₂(CHCH=CMe₂)⁺ (16.0 and 8.2 ppm).[27] Our ability to obtain a well-resolved NMR spectrum and our failure to observe an EPR signal for **3b²⁺** confirms that this species is diamagnetic.

In summary, the first members of a new class of mixed-valence complexes with polyenediyl bridges have been prepared and shown to have delocalized structures. Insights can be gained by comparison both with other transition-metal mixed-valence complexes and with related organic structures, such as the polymethine radicals.[28] In addition, the complexes **1–3** are members of the multistage redox systems X(CH=CH)ₙX, a general class from which many organic examples have been characterized.[29,30]

(25) Potentials were internally referenced to cobaltocene(⁰/⁺), which was added at the end of each experiment. Values are reported relative to Fc⁰/⁺.

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