A Butadienediyl-Bridged Diiron Compound in Three Oxidation Levels

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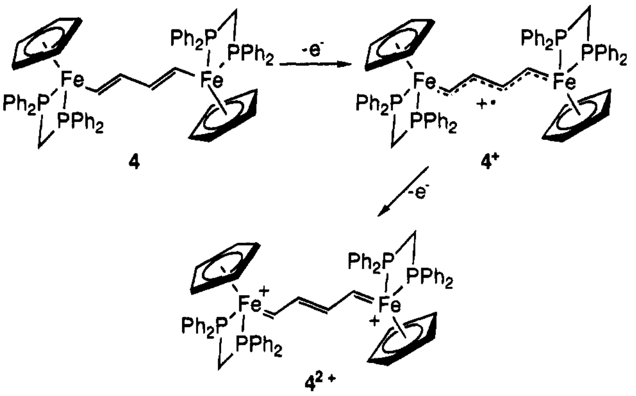
Summary: A conjugated dinuclear iron complex, $[CpFe(dppm)]_2(\mu\text{-}CH{=}CHCH{=}CH)$, *has been prepared and oxidized to radical cation and dication species. The butadienediyl bridge apparently allows for strong electronic coupling between the iron atoms, as determined by cyclic voltammetry, electronic absorption spectroscopy, and an X-ray crystal structure determination on the dication.*

In a recent communication,[1] we described the preparation of several butadienediyl-bridged diiron complexes, $[CpFe(CO)(L)]_2(\mu\text{-}CH{=}CHCH{=}CH)$ (**1**, L = CO; **2**, L = PMe_3; **3**, L = PPh_3; Cp = $\eta^5\text{-}C_5H_5$), and the oxidation of these neutral species to radical cation and dication species. The phosphine-substituted radical cations were designated as delocalized (class III) mixed-valence[2] ions on the basis of electron paramagnetic resonance (EPR) and IR spectra. More complete characterization of the oxidized species was hindered by their thermal instability. In this paper, we report the preparation of a related complex, $[CpFe(dppm)]_2(\mu\text{-}CH{=}CHCH{=}CH)$ (**4**, dppm = $\eta^2\text{-}Ph_2PCH_2PPh_2$; Scheme 1), whose oxidized forms ($\mathbf{4}^+$ and $\mathbf{4}^{2+}$) are both stable at room temperature. This work also complements recent reports concerning related complexes with other conjugated bridges.[3]

The neutral **4**[4] was prepared by photochemical substitution of **1**.[5,6a] The increased number of phosphine donors allowed for improved thermal and air stability of the oxidized forms of **4**, while the neutral species required more careful handling than did **2** or **3**, undergoing facile oxidation to $\mathbf{4}^+$ in the presence of trace amounts of oxygen. The dication $\mathbf{4}^{2+}$ was the most conveniently handled oxidation level, being stable to air in solution at room temperature for a day or two. Compound **4** exists as a single diastereomer, in contrast to compounds **2** and **3**.[1]

Scheme 1



Oxidation products $\mathbf{4}^+$ (pink-purple in solution) and $\mathbf{4}^{2+}$ (deep purple) were prepared by the reaction of **4** and 1 or 2 equiv of ferrocenium hexafluorophosphate ($FcPF_6$) in dichloromethane at 0 °C. The hexafluorophosphate salts were precipitated by addition of pentane.[6b]

Electronic absorption spectra[7] of $\mathbf{4}^+$ revealed bands at 518 nm (ϵ_{max} 10 000), 698 nm (ϵ_{max} 2000), and 1296 nm (ϵ_{max} 7000). The band at 1296 nm, which was not present in the spectra of **4** or $\mathbf{4}^{2+}$, was assigned as an intervalence charge-transfer band. This band had a width at half-maximum ($\Delta\nu$) equal to 2380 cm^{-1}. This value is less than the value predicted by Hush theory, 4220 cm^{-1}, consistent with a ground-state delocalized structure for the mixed-valence species.[2b,8] The electronic spectrum of **4** showed no maxima in the visible or near-IR region, while the spectrum of $\mathbf{4}^{2+}$ had a band at 546 nm (ϵ_{max} 30 000).

The EPR spectrum of $\mathbf{4}^+$ in dichloromethane showed a single band with no observable coupling and $g = 2.039$. This signal decayed only slightly over 1 h at room temperature. From the width of this band,[9] we estimated an upper bound for a_P of 3 G (assuming equal coupling to all four phosphorus atoms), while the isomers of $\mathbf{3}^+$ show coupling constants of 7 and 8 G.

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[1] Etzenhouser, B. A.; Cavanaugh, M. D.; Spurgeon, H. N.; Sponsler, M. B. *J. Am. Chem. Soc.* **1994**, *116*, 2221–2222.

[2] (a) Robin, M. B.; Day, P. *Adv. Inorg. Chem. Radiochem.* **1967**, *10*, 247–422. (b) Creutz, C. *Prog. Inorg. Chem.* **1983**, *30*, 1–73. (c) *Mixed Valency Systems: Applications in Chemistry, Physics, and Biology*; Prassides, K., Ed.; Kluwer: Dordrecht, The Netherlands, 1991.

[3] Le Narvor, N.; Lapinte, C. *J. Chem. Soc., Chem. Commun.* **1993**, 357. Seyler, J. W.; Weng, W.; Zhou, Y.; Gladysz, J. A. *Organometallics* **1993**, *12*, 3802–3804. Zhou, Y.; Seyler, J. W.; Weng, W.; Arif, A. M.; Gladysz, J. A. *J. Am. Chem. Soc.* **1993**, *115*, 8509–8510. Field, L. D.; George, A. V.; Laschi, F.; Malouf, E. Y.; Zanello, P. *J. Organomet. Chem.* **1992**, *435*, 347–356. See also citations from ref 1. For oxidation studies of related mononuclear complexes, see also: Connelly, N. G.; Gamasa, M. P.; Gimeno, J.; Lapinte, C.; Lastra, E.; Maher, J. P.; Le Narvor, N.; Rieger, A. L.; Rieger, P. H. *J. Chem. Soc., Dalton Trans.* **1993**, 2575–2578. Cron, S.; Morvan, V.; Lapinte, C. *J. Chem. Soc., Chem. Commun.* **1993**, 1611–1612.

[4] Mp: 110–120 °C dec. ^1H NMR (300 MHz, C_6D_6): δ 3.20 (m, 2H), 3.99 (m, 2H), 4.33 (s, 10H), 5.99 (m, 2H), 6.17 (m, 2H), 6.87–7.51 (m, 40H). Anal. Calcd for $C_{64}H_{58}Fe_2P_4$: C, 72.33; H, 5.50. Found: C, 72.03; H, 5.41.

[5] All procedures were carried out under nitrogen or argon. A solution of 50 mg (0.12 mmol) of **1** (Sanders, A.; Giering, W. P. *J. Organomet. Chem.* **1976**, *104*, 67–78) and 99 mg (0.26 mmol) of dppm in 210 mL of tetrahydrofuran (distilled from sodium/benzophenone) was photolyzed for 40 min at 0 (or −20) °C with a 450 W Hanovia lamp. The solvent was evaporated, the residue was redissolved in 7 mL of toluene/benzene (6:1), and this solution was filtered. Pentane (10 mL) was layered on top of the solution, and the vial was cooled to −30 °C until a single phase was obtained. Compound **4** was obtained as a brown solid, which was recrystallized again from toluene/pentane, if necessary; yield 50 mg (38%).

[6] (a) Gimasa, M. P.; Gimeno, J.; Lastra, E.; Lanfranchi, M.; Tiripicchio, A. *J. Organomet. Chem.* **1991**, *405*, 333–345. (b) Note added in proof: Oxidation of **4** with silver tetrafluoroborate has been found to give cleaner samples of $\mathbf{4}^{2+}$.

[7] In dichloromethane at ambient temperature.

[8] Hush, N. S. *Prog. Inorg. Chem.* **1967**, *8*, 391–444.

[9] Peak-to-peak width was 8 G at room temperature and 18 G at −60 °C.

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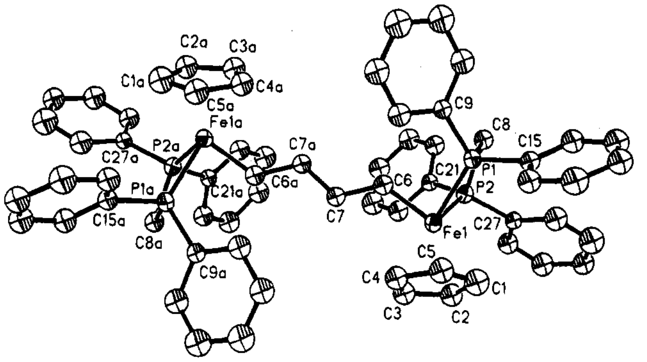

Figure 1. Molecular structure of 4^{2+}.

Fenske-Hall[10] calculations showed that the contribution of the phosphorus 4s orbital to the singly occupied MO is sensitive to the relative orientation of the bridge and the $CpFeL_2$ units. The calculation predicts a contact coupling of 5.8 G[11] when the bridge plane bisects the diphosphine ligand and 1.1 G when the bridge is rotated by 90°.[12] These results suggest that the variation in coupling constants among 3^+ and 4^+ might be due to differences in the distribution of conformers.

As for **2** and **3**,[1] the cyclic voltammogram of **4** showed two well-separated, reversible oxidation waves. The $E^{\circ\prime}$ values at 0 °C were -1.17 and -0.73 V.[13] The separation of 440 mV between these waves, similar to the values found for **2** and **3**, in indicative of a high comproportionation constant (3×10^7) and strong coupling between the metal centers. Identical cyclic voltammograms were obtained for samples of **4** and 4^{2+}, as well as for 4^+ prepared through bulk electrolysis.[14]

The bis(carbene) nature of 4^{2+} suggested in Scheme 1 is supported by the ^1H NMR spectrum.[15] Signals at 13.7 and 7.0 ppm corresponding to the bridge protons were observed, compared to values of 16.7 and 12.9 ppm for 3^{2+}.[1,16] The differences may be due to a combination of charge distribution and aniostropic shielding effects.[17]

An X-ray crystal structure was obtained for $4^{2+}(PF_6^-)_2{\cdot}4CH_2Cl_2$ (Figures 1 and 2). The compound crystallized from dichloromethane/pentane in the *C*2/*c* space group.[18] The X-ray structural study revealed the presence of the discrete dication 4^{2+}, two PF_6^- counterions, and four dichloromethane molecules of crystallization. The structure of the dication consists of two organoiron units linked by a butadiene-1,4-diyl bridge. The dication possesses a crystallographic 2-fold axis of rotation. Table 1 summarizes the bond lengths and angles, and more complete details of the structure are available as supplementary material.

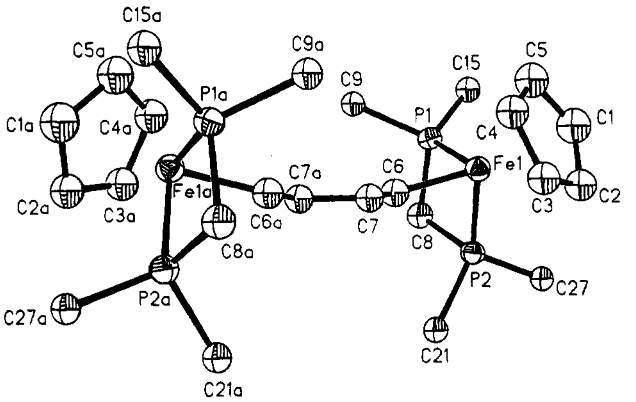

Figure 2. Molecular structure of 4^{2+}. All phenyl carbon atoms, except the *ipso* carbons, have been removed for clarity.

Table 1. Selected Bond Lengths (Å) and Angles (deg) for 4^{2+}

Fe(1)–C(6)	1.841(11)	Fe(1)–Cp[a]	1.748
Fe(1)–P(1)	2.198(3)	C(6)–C(7)	1.418(14)
Fe(1)–P(2)	2.198(3)	C(7)–C(7a)	1.366(20)
Fe(1)–C(6)–C(7)	129.1(7)	C(6)–Fe(1)–Cp	128.2
C(6)–C(7)–C(7a)	122.5(10)	P(1)–Fe(1)–Cp	131.7
C(6)–Fe–(1)–P(1)	88.4(3)	P(2)–Fe(1)–Cp	128.5
C(6)–Fe(1)–P(2)	88.2(3)	P(1)–Fe(1)–P(2)	74.5(1)

[a] Cp = centroid of the five carbon atoms, C(1)–C(5).

The Fe–C–C–C–C–Fe π system of the dication has an *all-trans* geometry. The four carbon atoms are nearly coplanar (the C6–C7–C7a–C6a dihedral angle is 170.0°), but the iron atoms are more significantly bent out of plane (the Fe–C6–C7–C7a dihedral angle is 161.8°). The crystal structure also shows that the phenyl groups of the dppm ligand serve to effectively shield the bridge, probably contributing to the stability of 4^+ and 4^{2+}.

The central C7–C7a bond of the dication (1.366 Å) is shorter than the flanking (C6–C7) bonds (1.418 Å), as expected for the bis(carbene) structure of Scheme 1. However, the bond lengths differ only by 0.05 Å, compared to 0.14 Å for 1,3-butadiene.[19] This suggests that the π bonds are not completely localized as depicted. Delocalization is supported by a Fenske–Hall calculation for a simplified dication in the crystallographic geometry, in which the phenyl groups of the

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[10] Hall, M. B.; Fenske, R. F. *Inorg. Chem.* **1972**, *11*, 768–775.

[11] One must treat these calculated values with caution, but the trend is probably meaningful. Calculated coupling constants were obtained by multiplying the 4s contribution to the singly occupied MO by the atomic orbital coupling of 3632 G. Gordy, W. *Theory and Applications of Electron Spin Resonance*; Wiley: New York, 1980; p 602.

[12] The coupling was found to be relatively insensitive to replacement of one phosphorus with a carbonyl ligand or to angular variations of several degrees between the ligands.

[13] Potentials are reported relative to internal $Fc^{0/+}$. Both waves showed $i_{p,c}/i_{p,a}$ equal to 1.0 and ΔE_p values close to 60 mV, consistent with reversible one-electron-oxidation processes. Electrochemical experiments used dichloromethane as solvent and tetrabutylammonium hexafluorophosphate (0.11 M) as electrolyte. The concentration of 4^{2+} (or **4**) was 0.5 mM. The scan rate was 40 to 400 mV/s.

[14] Bulk reduction of 4^{2+} to 4^+ at 0 °C (-1.01 V) verified that the reduction process involves a single electron.

[15] ^1H NMR (acetone-d_6): δ 5.33 (s, 10H), 5.97 (m, 4H), 6.96 (m, 2H), 7.31–7.70 (m, 40H), 13.71 (m, 2H). We have so far been unable to obtain satisfactory ^{13}C NMR spectra of either **4** or 4^{2+}, presumably due to the presence of trace paramagnetic impurities such as 4^+ or Fc^+.

[16] The carbene CH in $[(\eta^5\text{-}C_5Me_5)Fe(\eta^2\text{-}Ph_2PCH_2CH_2PPh_2)(CHOMe)]^+PF_6^-$ produces a ^1H NMR signal at 12.3 ppm. Roger, C.; Toupet, L.; Lapinte, C. *J. Chem. Soc., Chem. Commun.* **1988**, 713–715.

[17] The X-ray structure of 4^{2+} shows that the α bridge protons are in the shielding region of two phenyl groups (closest H···C contact 2.9, 3.1 Å) and the β bridge protons are shielded by four phenyl groups (closest H···C contact 3.7–4.7 Å), although the average structure in solution may differ.

[18] Crystal data: $C_{68}H_{66}Cl_8F_{12}Fe_2P_6$, monoclinic, space group *C*2/*c*, $a = 12.183(2)$ Å, $b = 19.024(4)$ Å, $c = 32.043(6)$ Å, $\beta = 98.99(3)°$, $V = 7335(4)$ Å^3, $D_c = 1.53$ g cm^{-3}, $\mu = 8.89$ cm^{-1}, $Z = 4$; 4800 unique data ($2\theta \leq 45.0°$) were collected at -50.0 °C on a Rigaku AFC5S diffractometer using Mo K_α ($\lambda = 0.710\ 73$ Å) radiation and 2θ–ω scan mode. The structure was solved by direct methods, and structural parameters were refined using full-matrix least-squares techniques to $R = 0.0686$ and $R_w = 0.0752$ for 2549 reflections having $F_0 \geq 6\sigma(F_0)$. Idealized H atom positions were introduced in the final cycles of refinement, with C–H bond distances set to 0.96 Å.

[19] Almennigen, A.; Bastiansen, O.; Traetteberg, M. *Acta Chem. Scand.* **1958**, *12*, 1221–1225.

dppm ligand were replaced by hydrogen atoms. The π-overlap populations for C6–C7 and C7–C7a were 0.27 and 0.31, respectively, whereas the corresponding populations in 1,3-butadiene were 0.48 and 0.09. Comparison of the dication calculation with another for the neutral species at the same geometry shows the four-carbon bridge taking 27% of the net charge difference, accounted for almost entirely by p_π orbitals.[20]

Previous theoretical studies focusing on related neutral complexes with alkenyl,[21] alkynyl,[22] or aromatic[23] ligands have shown that the principal π interaction is a repulsive, filled–filled interaction that serves to increase the energy of the appropriate π-type d orbital, making it the highest occupied MO. On the basis of the straightforward analogy (and on our own Fenske–Hall calculations) the situation is similar for **4**. When the neutral complex is oxidized, electrons are removed from the antibonding orbital, which makes the π interaction bonding. The presence of the strongly donating diphosphine allows also for an appreciable bonding interaction between the filled d_π and bridge π^* orbitals. Our calculation shows the lowest bridge π^* orbital to have a Mulliken population of 0.4 e in all three oxidation levels, while the highest bridge π orbital is depopulated from 2.0 e in the neutral to 1.5 e in the dication.

In summary, the π-conjugated butadienediyl bridge plays an important role in the bonding changes upon oxidation of **4**.

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Supplementary Material Available: Tables of crystal data, data collection, and structure solution details, atomic coordinates, bond lengths and angles, anisotropic temperature factors, and calculated hydrogen positions (9 pages). Ordering information is given on any current masthead page.

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[20] The iron atoms together take less than 4% of the net charge, with the balance being taken by the Cp (39%) and the $H_2PCH_2PH_2$ (31%) ligands.

[21] Kostic, N. M.; Fenske, R. F. *Organometallics* **1982**, *1*, 974–982.

[22] Lichtenberger, D. L.; Renshaw, S. K.; Bullock, R. M. *J. Am. Chem. Soc.* **1993**, *115*, 3276–3285. Lichtenberger, D. L.; Renshaw, S. K. *Organometallics* **1993**, *115*, 3522–3526. Frapper, G.; Kertesz, M. *Inorg. Chem.* **1993**, *32*, 732–740.

[23] Richardson, N. A.; Hall, M. B. *Organometallics* **1993**, *12*, 1338–1343.