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(Fulvalene)diiron Chemistry: Bis Piano-Stool Complexes and Their Redox Properties

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Summary: Photolysis of $[Fe_2Fv(C_6H_6)_2]^{2+}(PF_6^-)_2$ (**1**, Fv = μ_2-η^{10}-fulvalene) in MeCN with visible light at −15 °C in the presence of dppe or dppm ($\mathrm{P}\frown\mathrm{P}$) gives $[Fe_2Fv(\mathrm{P}\frown\mathrm{P})_2(MeCN)_2]^{2+}(PF_6^-)_2$ (**2a**, $\mathrm{P}\frown\mathrm{P}$ = dppe; **2b**, $\mathrm{P}\frown\mathrm{P}$ = dppm), which reacts with CO (1 atm) to give $[Fe_2Fv(\mathrm{P}\frown\mathrm{P})_2(CO)_2]^{2+}(PF_6^-)_2$ (**3a** and **3b**, respectively) and with PMe_3 to give $[Fe_2Fv(\mathrm{P}\frown\mathrm{P})_2(PMe_3)_2]^{2+}(PF_6^-)_2$ (**4**, $\mathrm{P}\frown\mathrm{P}$ = dppe). Oxidation of **4** by $(p\text{-}BrC_6H_4)_3N^+SbCl_6^-$ gives the delocalized mixed-valence tricationic complex **5**.

After a pioneering period mostly devoted to sandwich complexes,[1-3] fulvalene transition-metal chemistry has been recently shown to bear a fascinating potential of reactivity with a number of metals.[4-6] Diiron complexes are under focus in material science in view of their rich redox chemistry and have recently been involved in energy conversion.[1,5] We report here an entry to nonsandwich diiron fulvalene complexes presenting a rich electrochemistry and a delocalized $Fe^{II}Fe^{III}$ mixed valence.

We find that **1**[6] reacts with P donors in MeCN at −15 °C under photolysis with visible light[7] to give the dications $[Fe_2FvP_4(MeCN)_2]^{2+}$ (Scheme I). The reactions have been performed by using dppm or dppe. Only two phosphorus ligands can bind the metal, and the third coordination site is taken by the solvent MeCN. The resulting red acetonitrile complexes can be isolated, and **2a** and **2b** were characterized by using standard techniques.[8] These complexes react with CO or PMe_3 which replaces the acetonitrile ligand upon reflux (16 h) in 1,2-dichloroethane. This opens an easy, efficient route to yellow, crystalline, air-stable complexes of the type $[Fe_2FvP_4L_2]^{2+}(PF_6^-)_2$ (P_4 = $2\mathrm{P}\frown\mathrm{P}$) which were characterized by elemental analyses and spectroscopic techniques[9] (L = CO; **3a** (dppe) and **3b** (dppm); L = PMe_3, **4** (dppe); see Scheme I). The X-ray crystal structure[10] was solved for one of the two carbonyl complexes (dppm), and the ORTEP is shown on Figure 1.

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(8) Complex **2a**: 100 mL of a yellow MeCN solution of 1 (1 g, 1.5 mmol), containing partially soluble dppe (1.16 g, 3 mmol) in a Schlenk flask were degassed and photolyzed for 12 h at −15 °C with a 150-W visible lamp located at 1 cm from the Schlenk tube. The solution progressively turned red while the suspended solid disappeared. The solution was then concentrated to 20 mL, and addition of 100 mL of ether precipitated the complex **2a**. Recrystallization in acetone provided 1.82 g (88.7%) of air-stable red crystals of **2a**. Anal. Calcd for $C_{66}H_{62}N_2Fe_2P_6F_{12}$: C, 56.25; H, 4.40. Found: C, 55.98; H, 4.31. ^1H NMR (CD_3CN, TMS); δ 7.56 (m, 40 H, C_6H_5), 5.06 and 3.70 (2t, 8 H, Fv), 2.60 (m, 8 H, CH_2), 2.04 (s, 6 H, CH_3). ^{31}P NMR (C_6D_6O, H_3PO_4): δ +94.90 (s, dppe). Complex **2b** is synthesized similarly. Calcd for $C_{64}H_{58}N_2Fe_2P_6F_{12}$: C, 55.65; H, 4.20. Found: C, 55.39; H, 4.25. ^1H NMR (CD_3CN, TMS): δ 7.54 (m, 40 H, C_6H_5), 5.10 and 4.15 (2t, 8 H, Fv), 2.70 (m, 4 H, CH_2). ^{31}P NMR (C_3D_6O, H_3PO_4): δ 34.24 (s, dppm).

(9) Complex **3a**: a 1,2-dichloroethane solution (30 mL) of **2a** (1 g, 0.7 mmol) was degassed and refluxed under 1 atm of CO for 16 h. The red solution progressively turned yellow. The solvent was then removed under vacuum, and the solid residue was chromatographied on an alumina column with acetone as the eluent. Recrystallization from acetone/ether provided 0.84 g (86%) of yellow microcrystals of **3a**. Anal. Calcd for $C_{64}H_{56}O_2Fe_2P_6F_{12}$: C, 55.57; H, 4.05. Found: C, 55.57; H, 3.99. ^1H NMR (C_3D_6O, TMS): δ 7.69 (m, 40 H, C_6H_5), 6.04 and 5.05 (2t, 8 H, Fv), 3.05 (m, 8 H, CH_2). ^{31}P NMR (C_3D_6O, H_3PO_4): δ 91.04 (s, dppe). Infrared (1,2-$C_2H_4Cl_2$): ν_{CO} 1960 cm^{-1}. Complex **3b**: in a 250-mL autoclave were introduced 50 mL of 1,2-$C_2H_4Cl_2$ and 0.85 g (0.6 mmol) of **2b**. The solution was degassed and CO was introduced (180 atm). The autoclave was then heated for 15 h at 100 °C. The resulting yellow solution contained crystals. The mixture was chromatographied and recrystallized as above, which provided 0.72 g (86%) of yellow microcrystals of **3b**. Anal. Calcd for $C_{62}H_{52}O_2Fe_2P_6F_{12}$: C, 54.95; H, 3.98. Found: C, 54.84; H, 3.88. ^1H NMR (C_3D_6O, TMS): δ 7.52 (m, 40 H, C_6H_5), 5.86 and 5.35 (2t, 8 H, Fv), 4.50 (m, 4 H, CH_2). ^{31}P NMR (C_3D_6O, H_3PO_4); δ 25.56 (s, dppm). ^{13}C NMR (C_3D_6O): δ 216.33 (t, CO) 171.96 and 129.50 (m, C_6H_5), 92.04 (s, C, Fv), 83.95 and 81.32 (2s, CH, Fv), 43.21 (t, CH_2). Infrared (1,2-$C_2H_4Cl_2$): ν_{CO} 1970 cm^{-1}). Complex **4**: in 40 mL of 1,2-$C_2H_4Cl_2$ was dissolved 0.6 g of **2a**, and 2 equiv of PMe_3 was added under Ar. The reaction mixture was allowed to react at 20 °C for 2 days, the solvent was removed under vacuum, and these operations were repeated twice to displace MeCN completely. The resulting complex 4 was washed with ether. Anal. Calcd for $C_{68}H_{74}P_8Fe_2F_{12}$: C, 55.2; H, 5.0. Found: C, 54.95, H, 5.11. ^1H NMR (CD_3CN, TMS): δ 7.50 (m, 48 H, C_6H_5), 4.70 and 4.00 (2m, 8 H, Fv), 2.10 (m, 8 H, CH_2), 0.65 (d, 18 H, PMe_3). ^{13}C NMR (DMSO): δ 137.57 (C_6H_5), 131.75, 130.14, 125.86 (C_6H_5 CH), 89.20 (Fv), 78.30 and 78.01 (Fv, CH), 27.83 (CH_2), 18.60 (PMe_3).

(10) Yellow crystals of **3b** were obtained by recrystallization from acetone at room temperature. Crystal data: $FeP_3F_6OC_{31}H_{26}$, monoclinic with space group $P2_1/n$ and unit cell dimensions a = 8.361 (9) Å, b = 23.354 (7) Å, c = 15.557 (12) Å, β = 91.07 (4)°, V = 3037 (8) Å^3, Z = 2, and d_{calcd} = 1.574 Mg/m^3. Data were collected on a Nonius CAD4 diffractometer (λ(Mo Kα) = 0.710 73 Å, T = 291 K) and gave 5457 reflections (2332 with $I > 3\sigma(I)$; R_{int} = 0.037). The structure was solved by direct methods (MULTAN) and difference Fourier and was refined to the final residuals R = 0.060 and R_w = 0.077.

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Scheme I

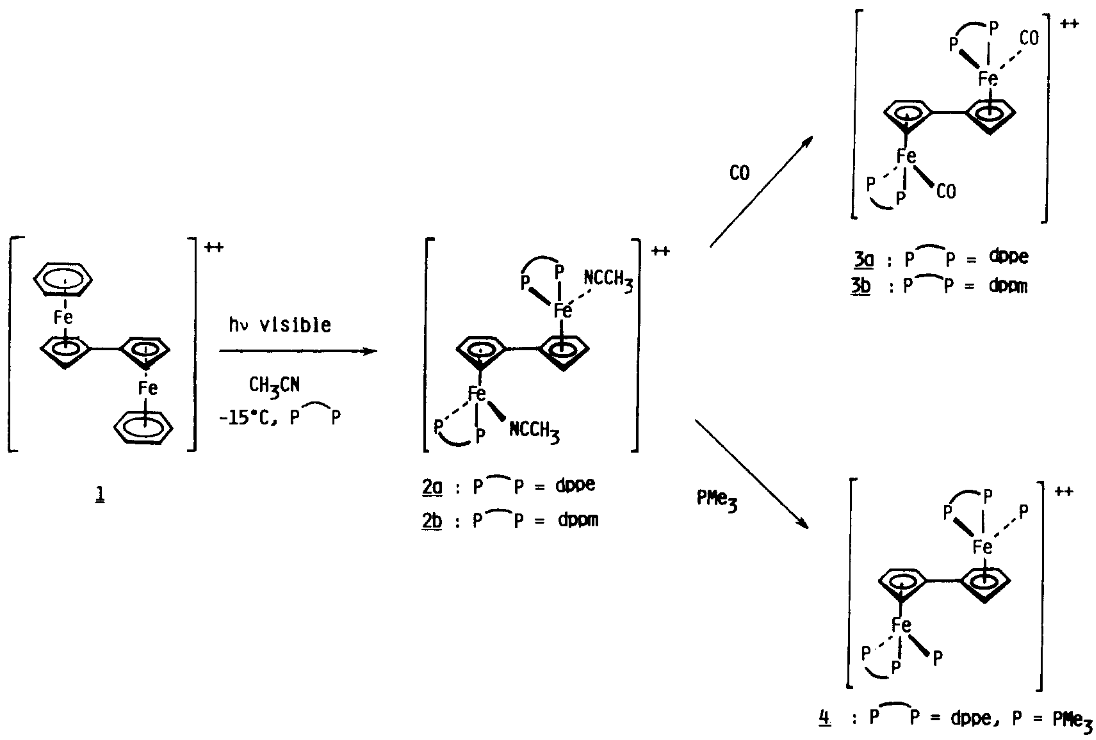

Table I. Electrochemistry of Binuclear Piano-Stool Diiron PF_6 Salts[a]

	E(ox.)		E(red.)	
$Fe_2Fv(dppe)_2(NCMe)_2^{2+}$ (**2a**)	+0.77 (irrev)	+1.12 (irrev)	−1.46 (irrev)	
$Fe_2Fv(dppm)_2(NCMe)_2^{2+}$ (**2b**)	+0.70 (irrev)			
$Fe_2Fv(dppe)_2(CO)_2^{2+}$ (**3a**)			−1.20	−1.32
$Fe_2Fv(dppm)_2(CO)_2^{2+}$ (**3b**)			−1.35 (irrev)	−1.47 (irrev)
$Fe_2Fv(dppe)_2(PMe_3)_2^{2+}$ (4)	+0.71	+0.95	−1.58 (irrev)	

[a] $E°$(rev) and E_p(irrev) values determined by CV vs SCE; Pt cathode; DMF; −30 °C; 1 M nBu_4NBF_4. Ferrocene is used as internal reference.

The two iron groups are located at each side of the planar fulvalene ligand.[11]

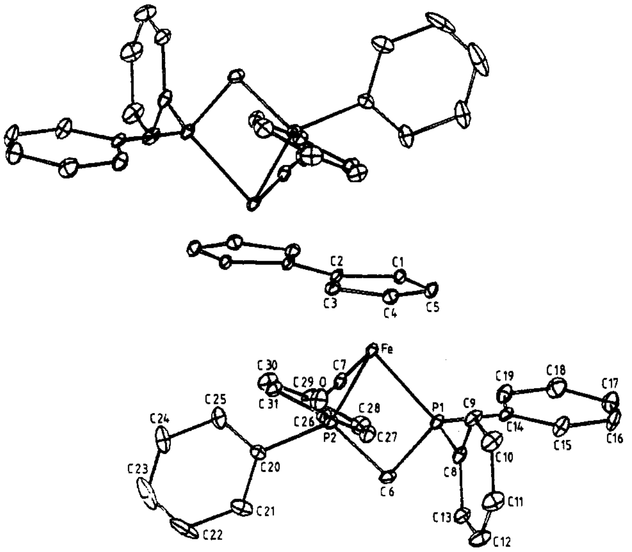

Figure 1. ORTEP view of the X-ray crystal structure of $[Fe_2Fv(dppm)_2(CO)_2]^{2+}(PF_6^-)_2$ (**3b**): mean Fe–Cp(centroid distance), 1.720 Å; C_p–C_p link, 1.459 (12) Å; mean P–C, 1.806 (7) Å; mean Fe–P, 2.199 (2) Å; Fe–CO, 1.762 (8) Å; ∠FeCO, 178.7 (6)°; ∠PFeP, 74.88 (7)°; ∠PCP = 93.2 (3)°.

The electrochemistry of the complexes is extremely dependent on the electronic properties of the ligands (Table I). The complex **2a** is oxidized at $E° = +0.77$ V vs SCE, and the cyclic voltammogram (CV) shows both chemical and electrochemical reversibility.[12] Thus the wave presumably represents a one-electron oxidation to the mixed-valence $Fe^{II}Fe^{III}$ state. A second oxidation wave at +1.12 V is highly chemically irreversible even at −30 °C. Cathodic reduction shows an irreversible wave at −1.46 V vs SCE. The complexes **3** are reduced on Hg in two reversible waves at −1.20 and −1.32 V vs SCE (even at 20 °C as indicated by combined CV[12a] and chronoamperometric studies).[12b] This behavior resembles that of the precursor complex **1** although the mixed-valence stabilization is larger in the sandwich (ΔE = 450 mV) than in the piano-stool series (ΔE = 120 mV). However, the analogy and the ΔE_p value (60 mV) are also in favor of two one-electron waves. Two more reduction waves with little reversibility

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[11] (a) $Fe_2Fv(PMe_3)_6^{2+}$ can also be made, but using a different route.[11b] (b) Lacoste, M.; Astruc, D., unpublished work.

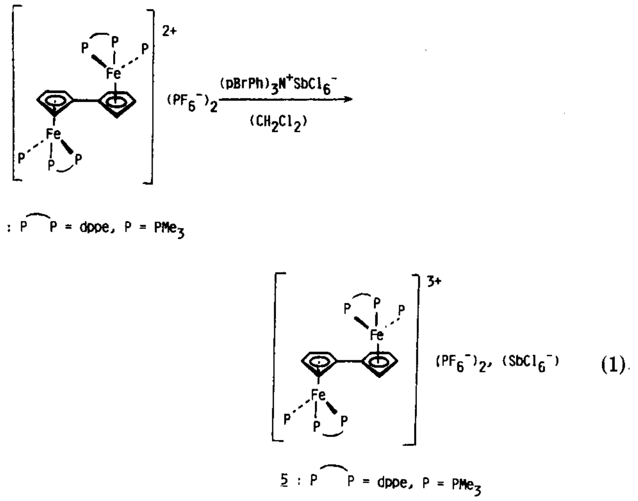
[12] (a) That the CV waves were diffusion-controlled was examined by verifying $i_p v^{1/2}$ = constant; chemical reversibilities were established when $i_{pa}/i_{pc} = 1$; electrochemical reversibility is mentioned in the text if E_{pa} and E_{pc} do not vary with scan rate and if $E_{pa} - E_{pc} = 0.06$ V, assuming one-electron waves (25 °C). (b) When two CV waves are too close, chronoamperometry establishes diffusion control and electrochemical reversibility; see: Bard, A. J.; Faulkner, L. R. *Electrochemical Methods*; Wiley: New York, 1980; Chapter 6.

Table II. Compared Mössbauer Data (77 K) of Fe^{II}, $Fe^{II}Fe^{II}$, Fe^{III}, and Mixed-Valence $Fe^{II}Fe^{III}$ Complexes (PF_6 Salts)[a]

	IS (mm s^{-1})	QS (mm s^{-1})
$Fe^{II}Cp(PMe_3)_3^+$	0.31	1.87
$Fe_2Fv(dppe)_2(PMe_3)_2^{2+}$ (**4**)	0.35	1.80
$Fe_2^{II}Fv(PMe_3)_6^{2+}$ (**6**)	0.32	1.76
$Fe^{III}Cp(PMe_3)_3^{2+}$	0.31	0.63
$Fe_2Fv(dppe)_2(PMe_3)_2^{3+}$ (**5**)	0.37	1.37
$Fe_2Fv(dppe)_2(PMe_3)_2^{4+}$ (**6**)	0.38	0.91

[a] All compounds give only one quadrupole doublet. Isomer shifts (IS) are given vs Fe metal, at room temperature. QS = quadrupole splitting.

are observed at −1.90 and −2.00 V vs SCE, and no oxidation wave is observed up to +1.50 V in the CV's. Complex **4** bearing six phosphorus ligands shows two chemically and electrochemically reversible oxidation waves at +0.71 and +0.95 V. Although complex **4** is very insoluble in the common polar solvents, we attempted to oxidize it by using $(p\text{-}BrC_6H_4)_3N^+SbCl_6^-$[13] in suspension in dichloromethane (eq 1). Mössbauer spectra of crude samples obtained by removal of the solvent under vacuum were made mainly of two quadrupole doublets corresponding to a mixed-valence $Fe^{II}Fe^{III}$ complex, **5** (Table II), and to a $Fe^{III}Fe^{III}$ complex together with signals corresponding to some decomposition to amorphous inorganic Fe^{III}. The Mössbauer spectra of **5** under zero field are essentially temperature independent and show a single quadrupole doublet (Table II), the parameters of which are intermediate between those of $[Fe^{II}Cp(PMe_3)_3]^+(PF_6^-)$ and $[Fe^{II}Cp(PMe_3)_3]^{2+}(PF_6^-)(SbCl_6^-)$, besides traces of unreacted **4** and amorphous inorganic Fe^{III}. That a single quadrupole doublet is found for the $Fe^{II}Fe^{III}$ complex with intermediate parameters between Fe^{II} and Fe^{III} indicates that, on the Mössbauer time scale (10^7 s^{-1}), this compound is a delocalized mixed-valence complex.[14]



Supplementary Material Available: Table of positional parameters, least-squares planes, dihedral angles between planes, distances between atoms, and thermal parameters for **3b** (13 pages); a listing of structure factors (14 pages). Ordering information is given on any current masthead page.

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(14) The mixed-valence complex $[Fe_2Fv(PMe_3)_6]^{3+}$ shows electrochemical and Mössbauer data similar to those of **5**.[11b]

Selective Catalytic Dehydrogenation of 1,4-Cyclohexadiene to Benzene. 1. Radical Anions Derived from Transition-Metal Arene Complexes as Promoters

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Summary: The reduction of 18e bis(arene) and arene–cyclodiene transition-metal complexes by potassium in dimethoxyethane has been applied to the generation of catalysts for the room-temperature aromatization of 1,4-cyclohexadiene.

Bis(arene)metal sandwiches are usually stable if they do not exceed an 18e count, the bis(hexamethylbenzene) d^7–d^8 group VIII metal complexes[1] being only apparent exceptions because distorsions may occur or the hapticity of one of the ligands may be reduced.

When the arene ligands are monocyclic and the metal possesses six d electrons, the sandwiches are generally inert toward ligand substitution reactions, which are facilitated instead when the system acquires an *extra* electron.[2] Such a labilization of one of the arenes is likely to proceed via the formation of an η^6-arene–η^4-arene complex observed in the case of the reduction of bis(benzene)chromium(0),[3] and this could explain why the bis(arene) d^7–d^8 group VIII metal complexes are rather labile.[1a,4]

These literature data, together with the reactivity of bis(arene) complexes of metals having more than six d electrons toward H–H and C–H bonds,[2,4a,5] have prompted us to pursue aromatic carbon–hydrogen bond activation by introducing an additional electron into neural bis(arene) group VI and arene–cyclodiene group VIII metal complexes. The catalytic aromatization of 1,4-cyclohexadiene under very mild conditions is reported here.

To bis(benzene)chromium(0)[6] (**1**) (0.36 mmol) and potassium sand (0.41 mmol) were added 1,2-dimethoxyethane, DME (25 mL), and 1,4-cyclohexadiene (5.3 mmol), and the mixture was stirred at 25 °C. This resulted in the total conversion of the diolefin to benzene and dihydrogen (GC);[7] the rate of evolution of the latter under atmospheric pressure increased during the first hour of reaction, reaching a value which corresponded to a turnover of 8.2

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(7) Cyclohexene was found only in trace amounts.

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