In summary, a potential model of the important S_2 state of the oxygen evolution enzyme has been obtained, based on the following similarities with the latter: (i) a metal nuclearity of four and the presence of oxide bridges; (ii) an average metal oxidation state of +3.25; (iii) two types of inequivalent Mn atoms; (iv) both "short" (av 2.814 Å) and "long" (av 3.285 Å) Mn⋯Mn separations (EXAFS data on S_1 indicate corresponding values of 2.69 (3) and ~3.3 Å[3b,13]); (v) observed spin states and hyperfine EPR features consistent with those of the native site.

Finally, terminal Mn–Cl linkages (av 2.266 Å) are not to be found in the native unit based on available data, and attempts to remove them from **1** are in progress, but whether a μ_3-Cl as found in **1** might be present is uncertain, especially given the long bond lengths (av 2.624 Å) which might make its spectroscopic identification more difficult. It is thus tempting to speculate whether such a μ_3-bridging requirement in some S_n states of the native system might be the origin of the recognized "Cl-dependence" of oxygen evolution.[14] Further studies are in progress, and additional Mn_4 species at this oxidation level are under characterization.[10,15]

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Supplementary Material Available: Fractional coordinates and isotropic and anisotropic thermal parameters (2 pages). Ordering information is given on any current masthead page.

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Organodiiron "Electron Reservoir" Complexes Containing a Polyaromatic Ligand: Syntheses, Stabilization, Delocalized Mixed Valences, and Intramolecular Coupling

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Transition-metal complexes with stable redox series have attracted attention recently because of their potential applications to technological devices.[1] Mononuclear organoiron sandwiches have already disclosed properties of electron-transfer (ET) catalysts.[2] We now report a novel series of diiron complexes of polyaromatics which can be reduced either in four single-electron steps or in a single two-electron step depending on the stereoelectronic design of the ligands. Also included are the first spectroscopic and structural characteristics of the bicyclohexadienylidene ligand.

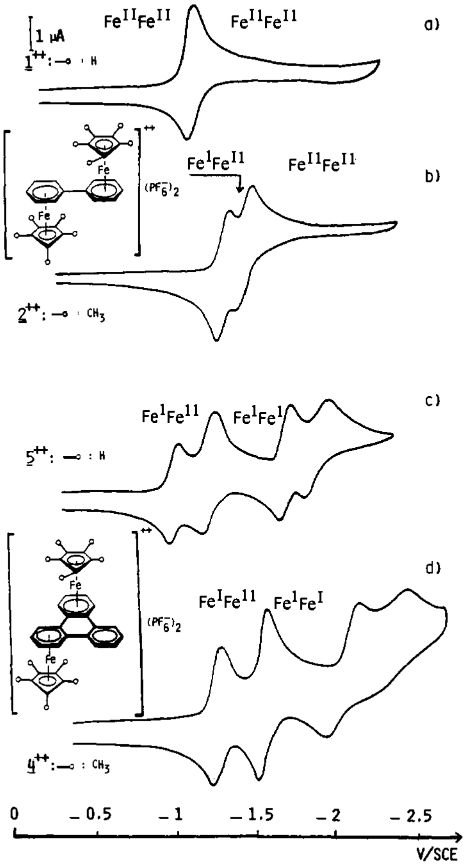

Figure 1. CV of the dicationic diiron complexes of biphenyl [(a) Cp, 1^{2+}; (b) Cp*, 2^{2+}] and of triphenylene [(c) Cp, 5^{2+}; (d) Cp*, 4^{2+}] at −35 °C with 0.1 M $n\text{-}Bu_4N^+BF_4^-$ on Hg cathode. Same trend on Pt. Internal standard: ferrocene. The CV's of 3^{2+} resemble those of 2^{2+} (b). For values of E_p, ΔE_p, and i_a/i_c, see text and supplementary material. E_p's vary with scan rates only for the fourth wave of 4^{2+} and 5^{2+} (slow ET).

We find that the cyclic voltammogram (CV) of the precursor $Fe^{II}Fe^{II}$ dication $[(FeCp)_2(biphenyl)]^{2+}(PF_6^-)_2$, 1^{2+},[3] shows, at −35 °C, only one two-electron wave (Figure 1a), i.e., the mixed valence $Fe^{I}Fe^{II}$ is not observable (at 20 °C, two waves were reported in the polarogram with ΔE = 100 mV[3a] which is now attributable to an EC mechanism). The reduction of $[Fe^{II}Cp(\eta^6\text{-arene})]^+PF_6^-$ by $LiAlH_4$ in THF −50 °C is known to result in ET:[4,5] $Fe^{II} \rightarrow Fe^{I}$. Applied to 1^{2+}, this reaction provides a deep blue, EPR-silent (4.2 K) solution of **1** (unstable above −30 °C) which, thus, cannot contain $Fe^{I}Fe^{II}$ or $Fe^{I}Fe^{I}$ species.[6] The working hypothesis is that a reversible structural and electronic rearrangement intervenes, concomitant to the second ET, and that the resulting energy gain lowers the potential of this second ET. Such a process is well documented in the $2e^-$ reduction of η^6-arene-Ru,[7] -Rh, -Ir,[8] and -Cr[9a] complexes to η^4-arene analogues,

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[§] Université de Rennes I (X-ray crystal structure).

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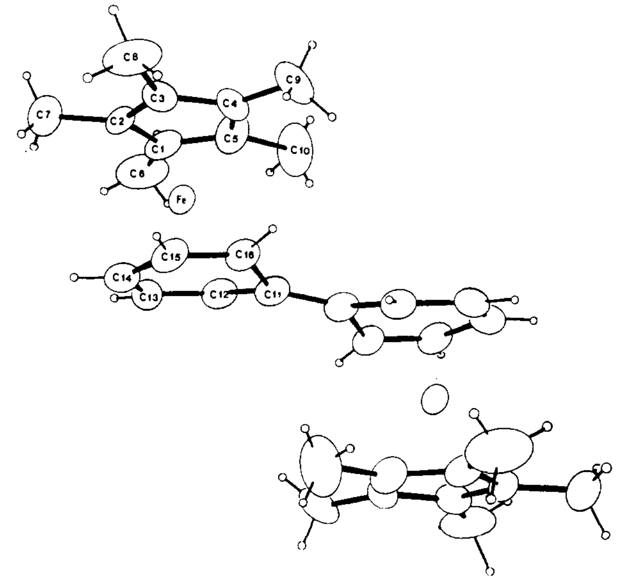
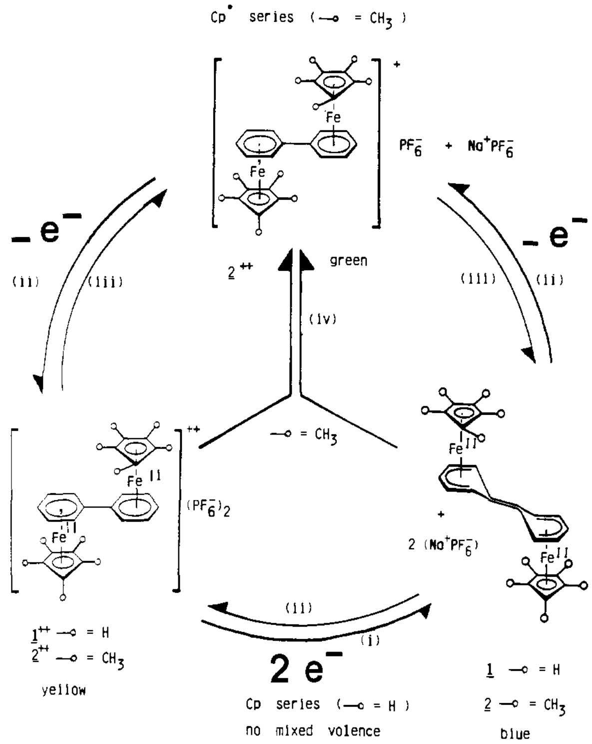


Figure 2. ORTEP view of the X-ray crystal structure of **2**.

and this hypothesis has been suggested in $[(CrCO)_3]_2$(biphenyl).[9b]

Fortunately, we also find that polyaromatics can be complexed in 30–40% yields by two $(FeCp^*)^+$ units ($Cp^* = C_5Me_5$) using $Cp^*Fe(CO)_2Br$[10] + Al_2Cl_6 in the melt or in an inert solvent[11] (110–140 °C, 2 days). The new dications $[(FeCp^*)_2(biphenyl)]_2^{2+}$, $\mathbf{2}^{2+}$, $[(FeCp^*)_2(9,10\text{-dihydrophenanthrene})]^{2+}$, $\mathbf{3}^{2+}$, and $[(FeCp^*)_2(triphenylene)]^{2+}$, $\mathbf{4}^{2+}$, were crystallized as PF_6^- salts.[12] Reduction of these salts by Na/Hg proceeds in THF ($\mathbf{2}^{2+}$ and $\mathbf{3}^{2+}$ at 20 °C, $\mathbf{4}^{2+}$ at −15 °C) in 2 h to give 65–80% yields of the very air-sensitive, neutral complexes **2**–**4** after recrystallization from toluene at −40 °C[12] (Scheme I). The ^1H and ^{13}C NMR spectra[12] of the thermally stable blue complexes **2** and **3** indicate a diamagnetic state with a novel bicyclohexadienylidene ligand also shown by the X-ray crystal structure[13] of **2** (Figure 2). The cyclohexadienyls have a folding angle of 25° and are linked by a double bond (1.37 Å; ^{13}C NMR δ (ppm) in C_6D_6, 101; **3**, 103) about which the substituents are at variance from planarity by 5°. Consistently, the Mössbauer spectra of **2** and **3** show temperature-independent quadrupole doublets, the parameters of which indicate an $Fe^{II}Fe^{II}$ state,[12] and an unusually large asymmetry parameter $\eta = 0.9$ detected under external field (6 T, 5 K). This coupled electronic structure is not obtained in the green triphenylene complex **4**, thermally stable up to 0 °C. The rigid plane of the latter inhibits the geometric variations above required by coupling, and this complex prefers to adopt the $38e^-$ Fe^IFe^I structure[6] (EPR at 77 K, $g_x = 2.0458$, $g_y = 2.0001$, $g_z = 1.8404$; Mössbauer data at 4.2 K, IS = 0.754 (3) mm s^{-1} versus Fe; Q.S. = 1.212 (1) mm s^{-1}, slight variation of Q.S. with T[14]).

Scheme I. ET Processes of Diiron Complexes of Biphenyl in THF[a]



[a] (i) $LiAlH_4$, −80 °C; (ii) O_2, $NaPF_6$; (iii) Na/Hg, 20 °C; (iv) conproportionation, 20 °C.

Interestingly, the CV's of these binuclear Cp* complexes all show two separated one-electron $Fe^{II} \rightarrow Fe^I$ waves, contrary to **1**. However, ΔE is smaller for $\mathbf{2}^{2+}$ (130 mV) and $\mathbf{3}^{2+}$ (160 mV) than for $\mathbf{4}^{2+}$ (290 mV) because energy gain in the second ET is not provided in the latter. The CV's of the triphenylene complexes $\mathbf{4}^{2+}$ and $\mathbf{5}^{2+}$ show, together, four chemically reversible one-electron waves (only the fourth wave indicates a slow ET) corresponding to formally $36\text{–}40e^-$ species (Figure 1). On the contrary, no cathodic reduction of **2** and **3** is observed down to −3 V versus SCE.

We were able to synthesize the green, thermally stable, air-sensitive mixed valence PF_6^- salts $\mathbf{2}^+$–$\mathbf{4}^+$ by mixing in THF equimolar amounts of the dication ($\mathbf{2}^{2+}$, $\mathbf{3}^{2+}$, or $\mathbf{4}^{2+}$) and of the neutral compound (**2**, **3**, and **4**) followed by recrystallization from acetone.[12] Alternatively, accurate titrations of **2** and **3** can easily be effected given the fast color change from blue (neutral) to green (mixed valence). The reactions are quantitative (conproportionation constants:[15] $\mathbf{2}^+$, 158; $\mathbf{3}^+$, 510; $\mathbf{4}^+$, 8×10^4). These complexes show a single, temperature-independent (from 4.2 to 293 K) quadrupole doublet in the zero-field Mössbauer spectra. The spectra of $\mathbf{2}^+$ under 6 T show a contact (Fermi) term of 6.7 T corresponding to $0.25e^-$ per iron, i.e. $0.5e^-$ per sandwich unit with 50% metal character. This indicates a *delocalized* mixed valence Fe^IFe^{II} state (class III)[16] and requires that, consistent with the CV data above, the structure of the biphenyl ligand be not intramolecularly coupled (since the bis-cyclohexadienylidene ligand, as shown in the X-ray structure, involves disruption of the π conjugation).

The THF solutions of the neutral complexes **2**–**4** still containing soluble $Na^+PF_6^-$ react instantaneously with $^1/_2$ mol of O_2, giving

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(12) Analytical and spectroscopic data for $(\mathbf{2}\text{–}\mathbf{4})^{2+/+/0}$ and $\mathbf{5}^{2+}$: supplementary material.

(13) Blue, air-sensitive crystals were obtained by crystallization from toluene at −40 °C. Crystal data: $FeC_{16}H_{20}$, monoclinic, $P2_{1/C}$, $a = 7.980$ (5) Å, $b = 21.757$ (9) Å, $c = 8.475$ (4) Å, $\beta = 113.35$ (4)°, V = 1350.9 (9) $Å^3$, $Z = 2$, $\mu = 4.3$ cm^{-1}, $D_c = 1.32$ $mg{\cdot}m^{-3}$. Data collection on a Enraf-Nonius diffractometer (λ (Mo $K\alpha$) = 0.710 73 Å, scan $w/2\theta = 1$, $t_{max} = 60$ s) gave 2626 reflections (1120 with $I > \sigma(I)$: $R_{int} = 0.033$). The structure is solved by using the Patterson method and several Fourier differences. After isotropic ($R = 0.080$) and anisotropic ($R = 0.054$) refinements, the H atoms are located in the same Fourier (between 0.39 and 0.21 e A^{-3}). Best refinement by complete matrix: $R = 0.056$; $R_w = 0.051$.

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$^1/_2$ mol of Na_2O_2 and the green mixed valence PF_6^- salts $\mathbf{2}^+$–$\mathbf{4}^+$, and then with another $^1/_2$ mol of O_2, giving the dicationic precursor PF_6^- salts $\mathbf{2}^{2+}$–$\mathbf{4}^{2+}$ (the presence of $Na^+PF_6^-$ inhibits the cage nucleophilic reactivity of $O_2^{\bullet -}$ on the sandwiches[17]).

In conclusion, this first series of bimetallic Cp*Fe complexes of polyaromatics provides electron reservoir complexes, stable in three oxidation states, in which the ligand structures control the coupling and the number of electrons transferred in a redox step.[18]

Acknowledgment. The experimental assistance of N. Ardoin, I. Rusig, Dr. W. Bowyer, and J.-G. Melin is acknowledged.

Supplementary Material Available: Spectroscopic, CV, and analytical data for $(\mathbf{2}\text{–}\mathbf{4})^{2+/+/0}$ and $\mathbf{5}^{2+}$ and tables of atomic positional and thermal parameters, bond lengths and angles, and general temperature factor expressions (6 pages); tables of calculated and observed structure factors (4 pages). Ordering information is given on any current masthead page.

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Intermolecular Vinylic C–H Bond Activation by a Doubly Bonded Organoditantalum Complex

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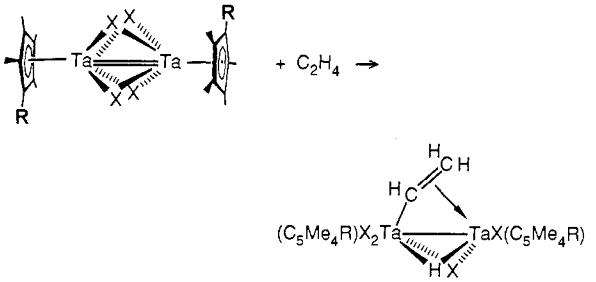
Intermolecular C–H bond activation of hydrocarbons, in particular alkanes, by organotransition-metal species is a reaction of fundamental modelling importance[1] for future efforts at hydrocarbon functionalization. Examples of hydrocarbon oxidative addition and of alkyl/hydrocarbon exchange have been reported with organometallic complexes of the late transition metals,[2] metals from groups 6[3] and 7,[4] and the lanthanides/actinides,[5] but there are no examples of intermolecular alkane or vinylic C–H bond activation with metals from groups 4 and 5. Intermolecular vinylic C–H bond activation is an underrepresented area in hydrocarbon C–H bond activation by organometallics, with few mononuclear[6] and dinuclear,[7] as opposed to polynuclear, examples. The kinetic and thermodynamic differences[8] between C–H activation involving the low-valent late metal and the high-valent lanthanide/actinide complexes suggest that intervening metal complexes, such as intermediate valent group 5 species, may exhibit optimal properties in C–H activation; the propensity for electronic unsaturation in complexes of these metals may lead to successful functionalization studies. Intramolecular ligand metalations[9] and arene H/D exchange reactions[10] with Nb and Ta complexes have been reported, and in principle intermolecular vinylic and alkane C–H bond reactivity should be feasible. We wish to report the first examples[11] of isolable *inter*molecular vinylic C–H activation by an early transition-metal (groups 4 and 5) organometallic and by a metal–metal multiply bonded complex.[12]

The reaction of the tantalum–tantalum doubly bonded complex $(\eta\text{-}C_5Me_4R)_2Ta_2(\mu\text{-}X)_4$[13] (**1a**, R = Me, X = Cl; **1b**, R = Me, X = Br; **1c**, R = Et, X = Cl; **1d**, R = Et, X = Br), prepared by the reductive dimerization of $(\eta\text{-}C_5Me_4R)TaX_4$, with ethylene (50 psi, 25 °C, 1 h) in ether leads to formation of the ditantalum vinyl hydride **2** (eq 1) in 75–85% isolated yield on the basis of analytical and spectroscopic data.[14] The 360 MHz ^1H NMR spectrum of the crystalline organoditantalum compound (Figure 1) exhibits an ABMX pattern for the vinyl hydride resonances. The IR spectrum shows an absorption at 1480 cm^{-1} which is tentatively assigned to a bridging hydride mode (in the absence of labeling



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[14] **2b**: Mass spectrum (30 eV, direct inlet) *m/e* 980, Br_4 pattern; ^1H NMR (δ, 25 °C, C_6D_6) 9.31 (m, 1, Ta–CH_x, $^3J_{H_xH_m}$ = 6.6 Hz, $^3J_{H_xH_a}$ = 8.7 Hz, $^3J_{H_xH_b}$ = 11.7 Hz), 4.36 (d of t, 1, Ta–H_m–Ta, $^4J_{H_mH_a}$ = 2.2 Hz, $^4J_{H_mH_b}$ = 2.0 Hz), 3.07 and 2.92 (m, 2, CH_aH_b, $^2J_{H_aH_b}$ = 7.3 Hz), 2.32 and 2.09 (s, 30, Cp*, Cp*′); ^{13}C NMR (δ, 25 °C, C_6D_6, gated {^1H}) 214.7 (d, $^1J_{CH}$ = 144 Hz, Ta–CH), 124.5 and 120.2 (Cp*, Cp*′), 98.4 (dd, $^1J_{CH}$ = 142 Hz, $^1J_{CH}$ = 162 Hz, CH_aH_b), 13.6 and 12.3 (Me and Me′, $^1J_{CH}$ = 129 Hz). Anal. Calcd ($Ta_2C_{22}H_{34}Br_4$): C, 26.96; H, 3.50; Br, 32.61. Found (combustion with WO_3/V_2O_5): C, 26.49; H, 3.50; Br, 32.12. **2a**: ^1H NMR (δ, 25 °C, C_6D_6) 8.62 (m, 1, Ta–CH_x), 4.71 (d of t, 1, Ta–H_m–Ta), 3.27 and 3.14 (m, 2, CH_aH_b), 2.23 and 2.01 (s, 30, Cp*, Cp*′).

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