How to design a Fast Two-electron Transfer: Structural Rearrangement in the Second Electron Transfer provides Stabilization
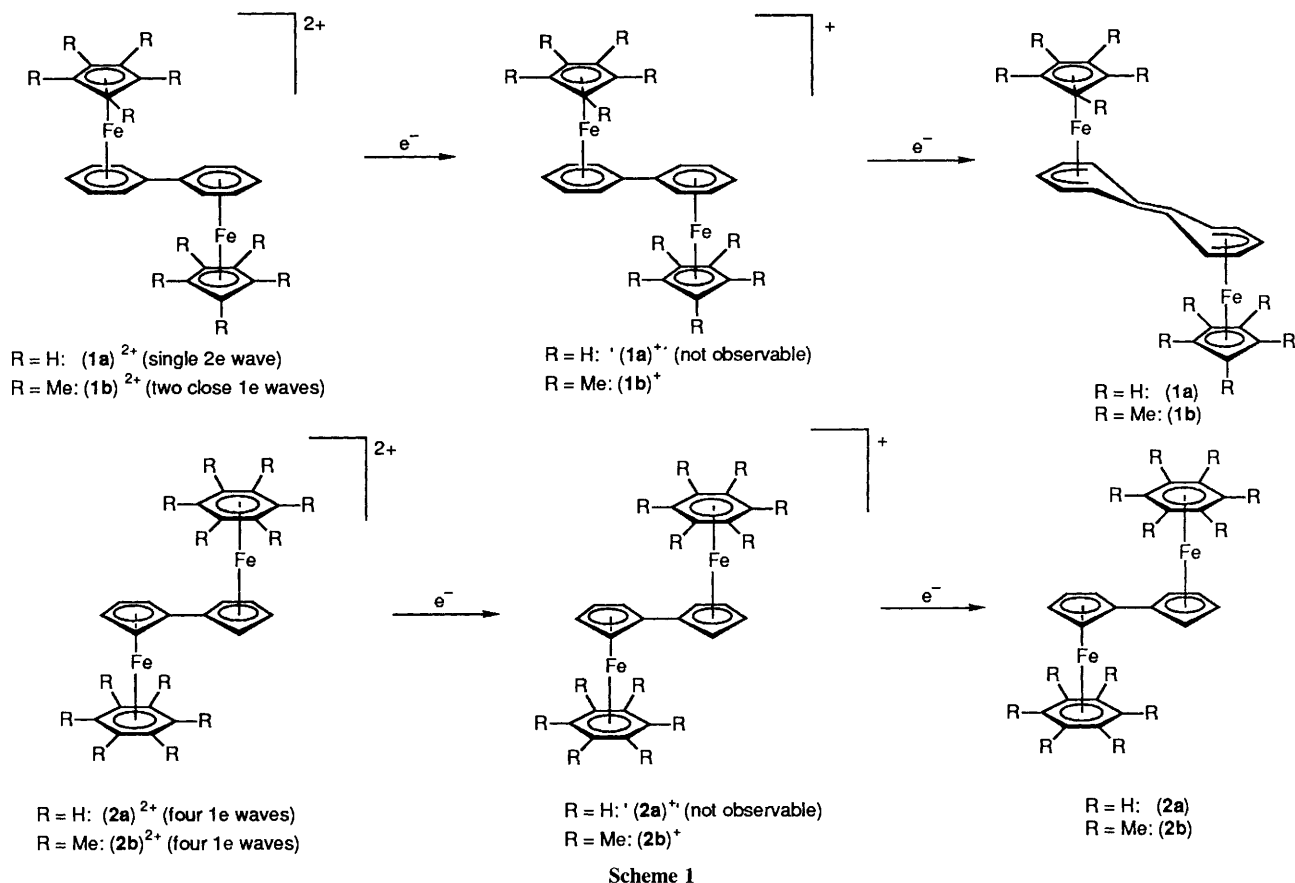
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The X-ray crystal structure of $[(FeC_5Me_5)_2(\mu_2,\eta^{10}\text{-biphenyl})]^+PF_6^-$, $(1)^+$, shows a 37-electron configuration indicating that the two-electron transfer $(1)^{2+}$ (36e) $\rightarrow$ $(1)^+$ (37e) $\rightarrow$ (1) (36e) proceeds with structural reorganization and stabilization in the second electron transfer.

The intimate mechanism of two-electron transfer (ET) processes has attracted the interest of theoreticians and experimentalists for many years.[1] Two-ET systems are useful redox mediators for energy conversion devices which require multi-electron steps, such as light-mediated water splitting.[2]

In these systems, structural characterization of the intermediate species resulting from the first ET is highly desirable. For instance, the reduction of a number of aromatic–transition metal complexes proceeds by two-ET with reduction of hapticity of the arene ligand.[3] However, no structural or even

R = H: (1a) $^{2+}$ (single 2e wave)
R = Me: (1b) $^{2+}$ (two close 1e waves)

R = H: '(1a)$^{+\cdot}$ (not observable)
R = Me: (1b)$^+$

R = H: (1a)
R = Me: (1b)

R = H: (2a) $^{2+}$ (four 1e waves)
R = Me: (2b)$^{2+}$ (four 1e waves)

R = H:'(2a)$^{+\cdot}$ (not observable)
R = Me: (2b)$^+$

R = H: (2a)
R = Me: (2b)

Scheme 1

spectroscopic information is available concerning the odd-electron intermediate and it is not yet understood why these systems proceed by two-ET.

Recently we have synthesized two isomeric series of binuclear electron-reservoir systems which link two FeCp-(arene) (Cp = C_5H_5) units either via the arene ligands in (1)[4a] or via the Cp ligands in (2).[4b,c] The two-electron reduction of (1a)$^{2+}$ occurs in one step with structural reorganization of the biphenyl ligand to a bicyclohexadienylidene, as already shown by X-ray analysis of (1b).[4a] Multiple one-electron reduction of (2)$^{2+}$, on the other hand, occurs without significant electronic or structural rearrangement at 20 °C to give the 38e Fe^{I}Fe^I species (2) (Scheme 1).[4b,c]

The X-ray structure of (1b)$^{+}$† shows an almost planar biphenyl ligand (Figure 1) indicating that the structural reorganization in (1) occurs in the second ET, not in the first one. This finding allows us to understand how and why a one-step two-ET operates.

Figure 1. Molecular structure of [(FeC$_5$Me$_5$)$_2$(μ$_2$,η^{10}-C$_{12}$H$_{20}$)]$^+$PF$_6^-$, (1)$^+$. Selected bond distances: C(21)–C(27) 1.487(15) Å, compare 1.37 Å in (1). Mean Fe–C(i) (i = 1—5) 2.86 Å; mean FeC(ii) (ii = 22—26) 2.06 Å; Fe(1)–C(21) 2.272(8). Folding angle of the biphenyl 5.5° [compare 25° in (1)]. The unit cell contains two independent molecules with similar characteristics and two acetone molecules. Compared X$_\alpha$ calculations rationalize the bonding in (1)$^+$ and (1).[6]

The structural reorganization indicates that (1) is more stable than an Fe^{I}Fe^I structure with a biphenyl ligand. The energy gain in this structural rearrangement can be estimated by comparison with the isomeric series (2) which does not rearrange upon two-ET. This comparison can be made using the thermodynamic potentials available from cyclic voltammetry. Indeed, all the reduction waves for (1) and (2) are fully
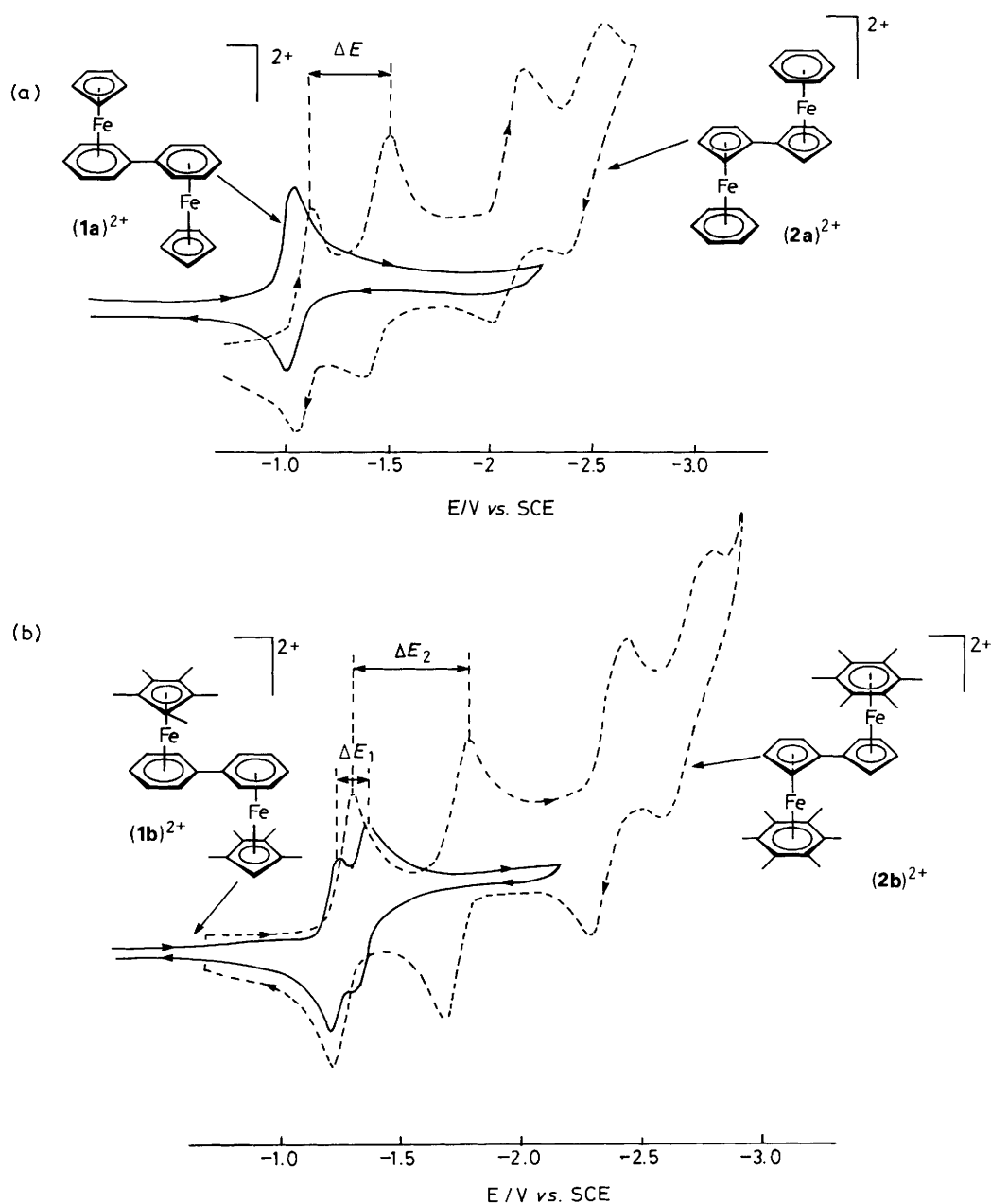
Figure 2. CV of (a) parent series, (1a) (——) and (2a) (————), and (b) permethylated series, (1b) (——) and (2b) (————) (3.3 × 10⁻⁵ M DMF solution; 0.1 M $[Bu^n_4N]^+[BF_4]^-$; Hg cathode; scan rate $0.4\,Vs^{-1}$; $-35\,°C$). Rearrangement energy ΔE [parent series (a)] and $\Delta E_2 - \Delta E_1$ [permethylated series (b)].

reversible both chemically and electrochemically (CV scan rate $0.4\,V\,s^{-1}$). The fact that the CV waves were diffusion-controlled was shown by verifying $i_p v^{-1/2} =$ constant. Thus, the structural rearrangements concomitant with the two-ET $(1a)^{2+} \rightarrow (1a)$ and with the ET $(1b)^+ \rightarrow (1b)$ are very fast. In the absence of significant structural reorganization [case (2)], the potential difference between the first two reduction waves is due to the variation in electrostatic interaction which depends on the charge and on the distance between the two redox centres, which is similar in $(1)^{2+}$ and $(2)^{2+}$. In the case of $(1a)^{2+}$, a two-electron wave was observed indicating that the energy gain due to the structural reorganization in the second ET fully compensates the electrostatic factor. This was not the case for $(1b)^{2+}$ (containing C_5Me_5 instead of Cp) where a small difference of 130 mV was observed between the two

reduction waves, characterizing the thermodynamic stabilization of $(1b)^+$. These trends lead us to estimate that $E°_{(1a)^{2+}/(1a)^+} \simeq E°_{(1a)^+/(1a)} \simeq -1.12\,V$ vs. saturated calomel electrode (SCE) [dimethylformamide (DMF), $Bu^n_4PF_6$, Hg cathode, $-35\,°C$]. Since $E°_{(2a)^{2+}/(2a)^+} = -1.15\,V$ vs. SCE and $E°_{(2a)^+/(2a)} = -1.47\,V$ vs. SCE, the difference $\Delta E° = E°_{(2a)^{2+}/(2a)^+} - E°_{(2a)^+/(2a)} = 0.32\,V$ can be attributed to the rearrangement $Fe^I Fe^I$ biphenyl $\rightarrow Fe^{II}Fe^{II}$ bicyclohexadienyl-idene: $\Delta G° = -0.32 \times 23 = -7.4\,kcal\,mol^{-1}$ (-30.9 kJmol⁻¹). In the case of $(2b)^{2+}$, the $\Delta G°$ value[5] is best estimated by comparison of the two permethylated series $(1b)^{2+}$ and $(2b)^{2+}$ [$\Delta E°_1 = 0.13\,V$ for $(1b)^{2+}$ and $\Delta E°_2 = 0.48\,V$ for $(2b)^{2+}$, thus $\Delta G° = (0.13 - 0.48) \times 23 = -8.1\,kcal\,mol^{-1} = -33.9\,kJ\,mol^{-1}$], see Figure 2.

We believe that all the cases where a reversible (fast) one

step two-ET was observed[3] follow a similar analysis, *i.e.*, are due to structural rearrangement which intervenes in the course of the second ET. Meanwhile, the examination of the thermodynamic redox potentials is useful in estimating the energy gain related to the structural reorganization. This view illustrates the idea that, in molecular chemistry, a fast two-ET is a succession of two one-ETs,[7] the second one occurring with $E°_2$ less negative than $E°_1$ (in the energy profile, the second ET may start later but be faster than the first one according to Marcus' theory[1a]).

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