Design of Bifunctional Organometallic 'Electron Reservoirs':[1] 35- to 38-Electron Sandwiches Including the First Stable, Localized Mixed Valence Complexes Containing Fe^I

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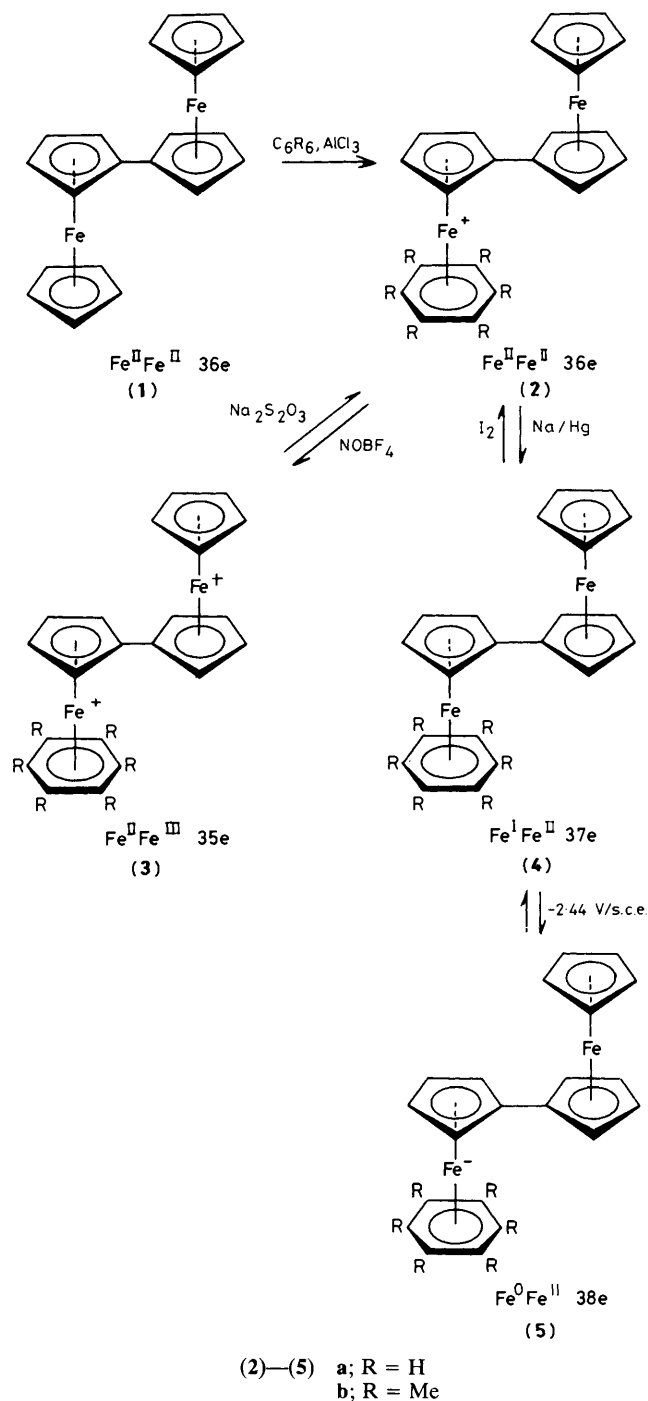
The new bimetallic complex $(cpFe)(cp-cp)(FeC_6Me_6)^+PF_6^-$, $(cp = C_5H_5)$ (2), synthesized from biferrocene and C_6Me_6, shows four oxidation states $(Fe^{III}Fe^{II})^{2+}$, $(Fe^{II}Fe^{II})^+$, $Fe^{II}Fe^{I}$, and $(Fe^{II}Fe^0)^-$ reversibly connected by cyclic voltammetry; the first three are stable and can be isolated and Mössbauer spectroscopy was used to investigate the electronic structure of the localized mixed valence $Fe^{II}Fe^I$.

There is much current research on redox catalysts which facilitate processes related to energy conversion.[2] In cases such as the photocatalytic splitting of water, redox catalysts are desirable for both oxidation and reduction within the same system.[3] It is possible that multivalent metal complexes could, in some instances, be used with redox catalysts for both oxidation and reduction. We report here the design, synthesis, and electronic structure of such bifunctional complexes, enabling us to delineate their potential utility.

The 18/19-electron sandwich complexes $(\eta^5-C_5H_4R)(\eta^6-C_6Me_6)Fe^{n+}$ $(n = 1, 0)$ are stable redox systems which can be used as 'Electron Reservoirs'.[4] We have examined the complementary activity of the 17/18 electron sandwich $(\eta^5-C_5H_5)_2Fe^{n+}$ $(n = 1, 0)$ as an oxidation electrocatalyst.[5] The coupling of these two structures gives a bimetallic system which will have three stable oxidation states providing the arene ligand is peralkylated. The desired new $Fe^{II}-Fe^{II}$ precursor (2b)† is obtained in 10% yield as red crystals from

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† (2b): ^1H n.m.r. $[(CD_3)_2CO, 20\ ^\circ C]$ δ 4.4 (m, 8H, cp–cp), 3.93 (s, 5H, cp), 2.33 (s, 18H, CH_3); ^{13}C n.m.r. $(CD_3CN, 20\ ^\circ C)$ δ 99.8 (C_6Me_6 ring), 96.9, 78.2, 75.9, 72.2, 69.9, 69.1 (cp–cp), 71.0 (cp), 17.6 (CH_3); Mössbauer (mm/s vs. Fe, 293 K) I.S. 0.39, Q.S. 2.27 (ferrocene); I.S. 0.43, Q.S. 1.89 {-cp($\eta^6-C_6Me_6)Fe^+$}. See also ref. 6.

$Fe^{II}Fe^{II}$ 36e
(1)

$Fe^{II}Fe^{II}$ 36e
(2)

$Na_2S_2O_3$ / NOBF$_4$

I_2 / Na/Hg

$Fe^{II}Fe^{III}$ 35e
(3)

Fe^IFe^{II} 37e
(4)

−2·44 V/s.c.e.

Fe^0Fe^{II} 38e
(5)

(2)—(5) a; R = H
         b; R = Me

Scheme 1

Figure 1. Cyclic voltammograms of (2b) in DMF at 20 °C (sweep rates: 0.5 V/s): (a) Oxidation: Pt anode, Bu_4NBF_4 0.1 M, (2b)⇌(3b): +0.61 V; (b) Reduction: Hg cathode, Bu_4NBF_4 0.1 M, (2b)⇌(4b): −1.58 V, (4b)⇌(5b): −2.36 V vs. s.c.e. (note the character of reversibility for this 20-electron Fe^0 centre).

Figure 2. Perturbation of the electronic structure of the mixed valence complex (4) by the ferrocene unit: temperature dependence of the Mössbauer quadrupole doublet (Fe^I centre). As a reference in $C_5R_5(\eta^6\text{-}C_6R_6)Fe^I$ (R = H, Me), Q.S. = $f(T)$ follows a regular law corresponding to a thermal population of the Kramers doublet.

equimolar amounts of biferrocene and C_6Me_6 and 2 mol of Al_2Cl_6, a synthesis which parallels that of the parent complex (2a)[6] (Scheme 1). The same reaction, effected with excess arene and Al_2Cl_6 leads to the bications $\{(\eta^5,\eta^5\text{-cp-cp})(Fe^{II} \eta^6\text{-arene})_2\}^{2+}$ (cp = C_5H_5) precursors of the average valence complexes.[7]

The voltammogram of (2b)[8—10]‡ shows three quasi-reversible waves even at 20 °C (Figure 1). On the Hg cathode

‡ The voltammogram of $cp(\eta^6\text{-}C_6H_6)Fe^+$ shows two quasi-reversible waves at −30 °C (ref. 9).
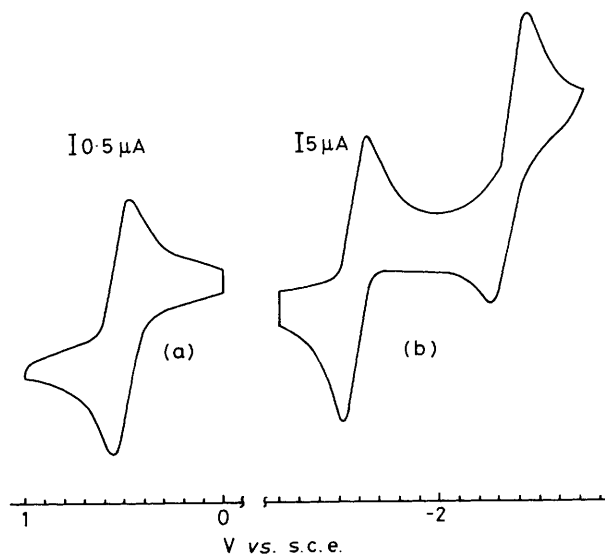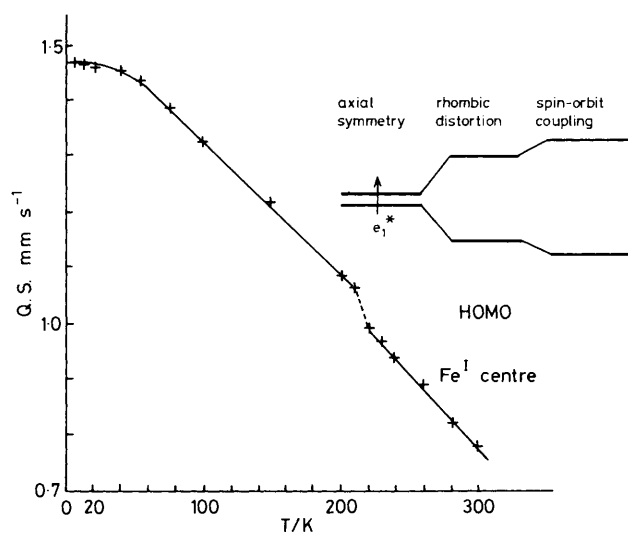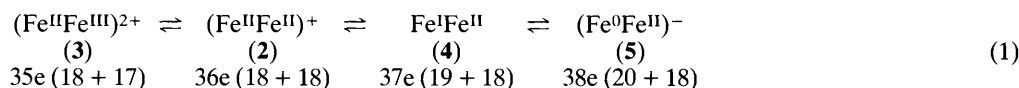
(dimethylformamide, DMF, Bu_4NBF_4, 0.1 M), the two reduction waves are observed at −1.58 and −2.36 V vs. standard calomel electrode, s.c.e., corresponding to the formation of the 37- and 38-electron sandwiches (4b) and (5b), [compare $cp(\eta^6\text{-}C_6Me_6)Fe^+$: −1.57 and −2.34 V vs. s.c.e., under the same conditions, the latter wave being reversible only at −30 °C]. The oxidation wave is observed at a Pt anode (DMF, Bu_4NBF_4, 0.1 M) at +0.61 V vs. s.c.e. (compare ferrocene +0.5 V vs. s.c.e.). Overall, four oxidation states are observed, equation (1). Since the reversibility of the reduction waves is lower for the parent complex (2a) (at 20 °C for the first wave, at −30 °C for the second one), the synthetic aspects were pursued in the permethyl series.

$$(Fe^{II}Fe^{III})^{2+} \; \rightleftharpoons \; (Fe^{II}Fe^{II})^{+} \; \rightleftharpoons \; Fe^{I}Fe^{II} \; \rightleftharpoons \; (Fe^{0}Fe^{II})^{-}$$

$$\begin{array}{cccc} \mathbf{(3)} & \mathbf{(2)} & \mathbf{(4)} & \mathbf{(5)} \\ 35e\,(18+17) & 36e\,(18+18) & 37e\,(19+18) & 38e\,(20+18) \end{array} \qquad (1)$$

Reaction of red (2b) with $NO^{+}BF_{4}^{-}$ in tetrahydrofuran THF ($-40\ ^{\circ}$C) gives NO and a colourless solution; pale green microcrystals are formed, analysing as the mixed valence dication (3b)§ which can be reduced back to (2b) by $Na_{2}S_{2}O_{3}$. Consistent with the $Fe^{II}Fe^{III}$ structure, the voltammogram of (3b) is the same as that of (2b) and its Mössbauer spectrum shows one doublet (Q.S. $= 2.4$ mm s^{-1}. I.S. $= 0.6$ mm s^{-1} vs. Fe) and a broad band (Q.S. $= 0.1$ mm s^{-1}. I.S. $= 0.5$ mm s^{-1} vs. Fe).[11]

$$cp(\eta^{6}\text{-}C_{6}Me_{6})Fe^{I}$$
$$\mathbf{(6)}$$
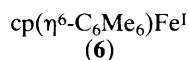
Reduction of (2b) in THF with 0.8% Na/Hg (1 h, 20 °C) gives thermally stable, extremely air sensitive ivory green crystals of the complex (4b) in 80% yield after recrystallization from pentane at $-80\ ^{\circ}$C. The e.s.r. spectrum in frozen THF at 77 K (10^{-5} mol 1^{-1}) shows three g values close to 2: $g_{y} = 2.065$, $g_{x} = 2.005$, and $g_{z} = 1.853$. This indicates a rhombic distortion of the Fe^{I} centre associated with the splitting of the degenerate $e_{1}{}^{*}$ level (Kramers' doublet) and the dynamic Jahn–Teller effect.[12] The presence of the ferrocene unit has a dramatic influence on the Mössbauer data. Whereas the spectrum of $cp(\eta^{6}\text{-}C_{6}Me_{6})Fe^{I}$, (6), shows two doublets at low temperature, that of (4b) shows only one doublet corresponding to the Fe^{I} unit in addition to the temperature independent ferrocene doublet (Q.S. $= 2.31$ mm s^{-1}, I.S. $= 0.43$ mm s^{-1} vs. Fe). The quadrupole splitting of the Fe^{I} doublet of (4b) is temperature dependent, which confirms a 19-electron Fe^{I} d^{7} structure,[4] but at variance with that of (6). The quadrupole splitting, Q.S., decreases progressively with increasing temperature between 4 and 300 K, in contrast to (6). This is best rationalized by the minimization of the interaction between the Fe^{I} units in the solid state due to the bulk of the ferrocenyl group and the perturbation introduced in the packing by anchoring an 'active' Fe^{I} centre to an 'inert' Fe^{II} one. This peculiar Fe^{I} electronic state allows observation of the thermal events occurring in the solid: in the case of (4b), the distortion is observed up to room temperature and the temperature dependence of Q.S. exhibits a break at 210—220 K suggesting a phase transition (Figure 2). These aspects should be clarified by the X-ray crystallographic study of (4b). Ham's parameter, p, of reduction of the spin-orbit coupling fits the temperature dependence of Q.S. with values significantly lower than 1 (p ca. 0.3 to 0.4), a separation of 400 ± 40 K of the Kramers doublet,[13] and ca. 80% metal character for the $e_{1}{}^{*}$ antibonding HOMO. The temperature dependence of Q.S. for the Fe^{I} doublet of this localized (Class 1)[14] mixed valence system contrasts with the temperature independent quadrupole doublet observed in delocalized mixed valence systems containing Fe^{I}.[7]

This is the first characterization of a localized mixed valence $Fe^{II}Fe^{I}$ complex. The good thermal stability of the three isostructural oxidation states in (2), (3), and (4) and the large difference between the two redox potentials (ca. 2.2 V) open the possibility of using this 3-oxidation state system as a bifunctional redox- and electrocatalyst. The Fe^{II}/Fe^{I} redox centre of (4b) acts as a stable redox catalyst for the rapid electroreduction of NO_{3}^{-} to NH_{3} in water on Hg, a general

property of the $cp(\eta^{6}\text{-arene})Fe^{n+}$ systems bearing a permethyl arene ligand.[15] The Fe^{II}/Fe^{III} redox centre of (3) acts as a stable oxidation electrocatalyst for the chelation of monodentate dithiocarbamate ligands in iron complexes.[5]

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§ The new, thermally stable complexes (2b), (3a), (3b), and (4b) gave satisfactory C, H analyses.