Electronic Communication and Switching between two Iron Atoms across the Phenanthrene–Dihydrophenanthrene Bridging Ligands

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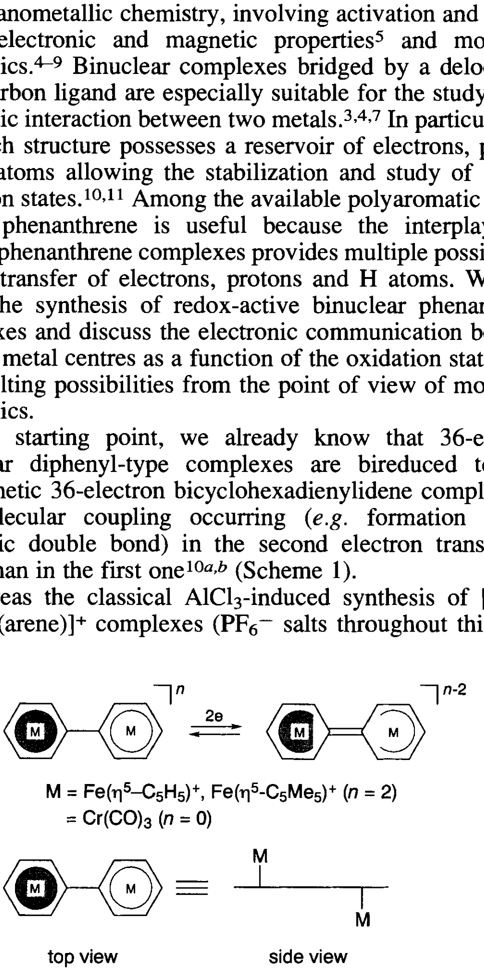
The complexes $[\{Fe(\eta^5\text{-}C_5Me_5)\}_2(\mu_2,\eta^{12}\text{-phenanthrene})]^{n+}$ have been synthesized for n = 0–2; the green 37-electron mixed-valence Fe^IFe^{II} monocation is delocalized on the Mössbauer time-scale at 4 K and the bireduced neutral complex has a triplet Fe^IFe^I state for phenanthrene in contrast with the singlet $Fe^{II}Fe^{II}$ state for the dihydrophenanthrene complex; interconversion between the phenanthrene and dihydrophenanthrene series by contact with O_2 and H_2O makes this system a switchable molecular-electronic device.

Electron transfer and radical processes have recently emerged as an increasingly attractive area of transition metal inorganic and organometallic chemistry, involving activation and catalysis,[1–4] electronic and magnetic properties[5] and molecular electronics.[4–9] Binuclear complexes bridged by a delocalized hydrocarbon ligand are especially suitable for the study of the electronic interaction between two metals.[3,4,7] In particular, the sandwich structure possesses a reservoir of electrons, protons and H atoms allowing the stabilization and study of several oxidation states.[10,11] Among the available polyaromatic frameworks, phenanthrene is useful because the interplay with dihydrophenanthrene complexes provides multiple possibilities for the transfer of electrons, protons and H atoms. We now report the synthesis of redox-active binuclear phenanthrene complexes and discuss the electronic communication between the two metal centres as a function of the oxidation states, and the resulting possibilities from the point of view of molecular electronics.

As a starting point, we already know that 36-electron binuclear diphenyl-type complexes are bireduced to give diamagnetic 36-electron bicyclohexadienylidene complexes,[10] intramolecular coupling occurring (*e.g.* formation of the exocyclic double bond) in the second electron transfer[10d,e] rather than in the first one[10a,b] (Scheme 1).

Whereas the classical $AlCl_3$-induced synthesis of $[Fe(\eta^5\text{-}C_5Me_5)(arene)]^+$ complexes (PF_6^- salts throughout this communciation) using $[Fe(\eta^5\text{-}C_5Me_5)(CO)_2Br]$[10b] and dihydrophenanthrene gives pure **2**$^{2+}$ in 50% yield, phenanthrene yields a mixture of the phenanthrene and dihydrophenanthrene dinuclear complexes for which chromatographic separation turned out to be too tedious. We sought an alternative synthetic route to **1**$^{2+}$ and found that modification of this procedure by the addition of $Al_2Cl_3Me_3$[12] gave the pure phenanthrene complex in 40% yield without any hydrogenation (Scheme 2) as shown by ^1H and ^{13}C NMR spectroscopy.



M = $Fe(\eta^5\text{–}C_5H_5)^+$, $Fe(\eta^5\text{-}C_5Me_5)^+$ (n = 2)
= $Cr(CO)_3$ (n = 0)

Scheme 1

The cyclic voltammogram (CV) of **1**$^{2+}$ shows three fully reversible monoelectronic reductions ($E°$ = 1.170, −1.440, −1.990 V in DMF, −35 °C, Hg cathode) and a fourth wave which is only partly chemically and electrochemically reversible ($E°$ = −2.190 V). The slow electron transfer 39e → 40e indicates molecular rearrangement avoiding the presence of four electrons in the antibonding orbitals. This CV contrasts with that of $\{[Fe(\eta^5\text{-}C_5Me_5)\}_2(\mu_2,\eta^{12}\text{-dihydrophenanthrene})]^{2+}$ **3**$^{2+}$, which shows only two reversible one-electron waves. The bielectronic reduction of **2**$^{2+}$ gives a 36e complex analogous to the diphenyl case shown in Scheme 1. This dichotomy suggests that the bireduced complex **1** is not subject to this intramolecular coupling, as fulvalene[13a,b] and larger polyaromatic[13c] Fe^IFe^I complexes. Na–Hg reduction of **1**$^{2+}$ was effected in THF at −20 °C because of the thermal instability of **1** above −10 °C. This reaction yields the air-sensitive purple–brown complex **1** which indeed does not show ^1H NMR signals in the diamagnetic region, but discloses an EPR spectrum with three 3 g values around 2 (g_x = 2.0617, g_y = 2.0015, g = 1.8566) characteristic of Fe^I complexes.[13c] The triplet state is also confirmed by the Mössbauer spectra under a magnetic field and the quadrupole doublet at zero field shows a quadrupole splitting (Q.S.) very distinct from that of neutral Fe^{II} diamagnetic complexes such as **2** (see Table 1). This dramatic difference of coupling (magnetic *vs.* chemical) between the bireduced phenanthrene and dihydrophenanthrene complexes **1** and **2** is undoubtedly due to the

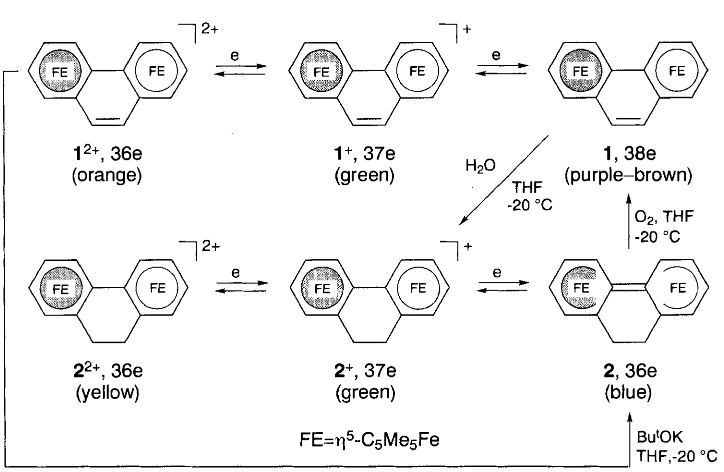
$$\begin{array}{l} 2[Fe(\eta^5\text{-}C_5Me_5)(CO)_2Br] \\ \quad + \text{phenanthrene} \end{array} \longrightarrow [\{Fe(\eta^5\text{-}C_5Me_5)\}(\mu_2,\eta^{12}\text{-phenanthrene})]^{2+}$$

Scheme 2 *Reagents and conditions*: Al_2Cl_6 + $Al_2Cl_3Me_3$, neat, 130 °C

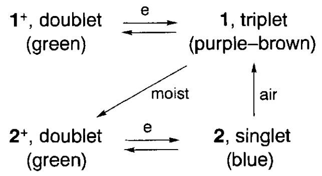
Table 1 Fitted Mössbauer parameters (mm s^{-1}) at 77 K for neutral, mono- and bi-reduced complexes **1**$^{n+}$ and **2**$^{n+}$ (n = 0–2)[a]

		Isomer shift (I.S.) *vs.* Fe	Quadrupole splitting (Q.S.)	Linewidth (Γ)
$[\{Fe(\eta^5\text{-}C_5Me_5)\}_2(\text{phenanthrene})]^{2+}$	**1**$^{2+}$	0.546(1)	1.374(1)	0.23(2)
$[\{Fe(\eta^5\text{-}C_5Me_5)\}_2(\text{dihydrophenanthrene})]^{2+}$	**2**$^{2+}$	0.549(1)	1.440(3)	0.290(2)
$[\{Fe(\eta^5\text{-}C_5Me_5)\}_2(\text{phenanthrene})]^{+}$	**1**$^{+}$	0.587(1)	1.310(3)	0.395(7)
$[\{Fe(\eta^5\text{-}C_5Me_5)\}_2(\text{dihydrophenanthrene})]^{+}$	**2**$^{+}$	0.544(1)	1.466(3)	0.514(5)
$[\{Fe(\eta^5\text{-}C_5Me_5)\}_2(\text{phenanthrene})]$	**1**	0.603(2)	1.312(3)	0.43(1)
$[\{Fe(\eta^5\text{-}C_5Me_5)\}_2(\text{dihydrophenanthrene})]$	**2**	0.593(1)	1.687(1)	0.256(2)

[a] Satisfactory elemental and spectroscopic analyses were obtained for the new compounds except for the thermally unstable complex **1**$^+$.



Scheme 3



Scheme 4

differences in flexibility between these two polyaromatics. The flexibility requirement for chemical coupling is met for **2**, not for **1**.

Reaction of **2** with O_2 in toluene at −20 °C gives a double H-atom abstraction yielding **1**, a reaction known to proceed *via* $O_2^{\bullet -}$ in the monoiron series.[11] Note that this oxidation leads here to a reduction $Fe^{II} \rightarrow Fe^{I}$ of the metal. Subsequent oxidation of **1** using 2 equiv. of $[Fe(\eta^5\text{-}C_5H_5)_2]^+$ gives $\mathbf{1}^{2+}$ and ferrocene. In this way, it is also possible to synthesize $\mathbf{1}^{2+}$ from $\mathbf{2}^{2+}$ in 30% overall yield (compare with the direct synthesis of $\mathbf{1}^{2+}$, Scheme 2). Deprotonation of $\mathbf{2}^{2+}$ using Bu^tOK[14] in THF also gives **1** {30% overall yield from $\mathbf{2}^{2+}$ to $\mathbf{1}^{2+}$ after oxidation using $[Fe(\eta^5C_5H_5)_2]^+$}, but filtration of $K^+PF_6^-$ is tedious. Equimolar amounts of **1** and $\mathbf{1}^{2+}$ react in THF at −20 °C to give the air-sensitive green mixed-valence complex $\mathbf{1}^+$. The single Mössbauer doublet from 4 to 300 K found for $\mathbf{1}^+$ shows that this compound has an average, delocalized valence on the Mössbauer time-scale (*ca.* 10^{-7} s^{-1}) in this temperature range. Indeed, this finding is consistent with the rather large difference in redox potentials between the first and second monoelectronic reductions,[15] $\Delta E° = 270$ mV. Although the difference between $E°_{2^{2+}/2^{+}}$ and $E°_{2^{+}/2}$ is only 160 mV, $\mathbf{2}^+$ is also delocalized on the Mössbauer time-scale. One may notice that there is very little difference in the Mössbauer parameters of the series $\mathbf{1}^{2+}/\mathbf{1}^{+}/\mathbf{1}$, which indicates that the 37th and 38th electrons are located in essentially phenanthrene orbitals. Finally, **1** reacts with H_2O at −20 °C in THF to give $\mathbf{1}^+$, isolated in 60% yield as a PF_6^- salt after addition of $Na^+PF_6^-$.

The system in Scheme 3 can be depicted in terms of a molecular-electronic device. Electron transfer to the green doublet $\mathbf{1}^+$ gives the purple–brown triplet **1** whereas electron-transfer to the green doublet $\mathbf{2}^+$ gives the blue singlet **2** which can give **1** in air whereas **1** gives $\mathbf{2}^+$ upon exposure to moisture (Scheme 4). Thus, the change of colour or of magnetic signal upon electron transfer (electric signal) can be switched either way upon contact with air or moisture. The colorimetric and magnetic changes can also monitor the presence of air or moisture.

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