Redox Chemistry of the Heterodinuclear Fulvalene Complexes [WM(fulvalene)(CO)$_5$], M = Fe or Ru: Selective Metal Redox Recognition

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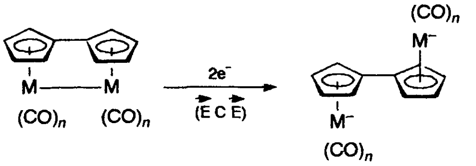
The redox chemistry of [WM(fulvalene)(CO)$_5$], M = Fe (**1**) and Ru (**2**) allows the specific redox properties of each metal centre to be distinguished.

One-electron oxidation of the 18-electron complex [Fe(C$_5$Me$_5$)$_2$] has provided the first example of a molecular ferromagnet.[1] It is likely that several other families of delocalized organometallic compounds should also show outstanding magnetic properties. Mononuclear complexes such as [Rh(C$_5$H$_5$)(CO)(PPh$_3$)] are known to dimerize upon oxidation to the fulvalene complexes.[2] Can this building block principle be applied to the dimerization of dinuclear fulvalene complexes? So far, fulvalene complexes[3] have posed well known mixed-valence problems[4,5] in bi-sandwich substrates and shown a rich organometallic chemistry,[6] including photorearrangements.[7] Bard and his colleagues[8] have examined the electrochemistry of a family of homodinuclear fulvalene compounds which, like the dimeric cyclopentadienyl analogues, undergo a two-electron reduction ($\overrightarrow{E}C\overrightarrow{E}$). Some heterodinuclear homologues follow the same trends[8] (Scheme 1).



Scheme 1 M(CO)$_n$ = Ru(CO)$_2$ or M(CO)$_3$ (M = Cr, Mo, W)

We now find that, in the complexes [WM(fulvalene)(CO)$_5$],[9] the two metals are either reduced or reoxidized at well separated potentials, as shown in the cyclic voltammograms (Figs. 1 and 2).

Table 1 compares the irreversible peak potentials for reduction and reoxidation of **1** and **2** with those of the

Table 1 Comparison of potential of homodimetallic[a] complexes and heterodimetallic[b] fulvalene carbonyl complexes

	E/V *vs.* SCE			
M-M	Red1	Red2	Reox2	Reox1
Ru-Ru[c]	−1.409		−0.259	
W-W[c]	−0.579		+0.166	
W-Ru[d]	−1.515		−0.700	−0.045
W-Fe[d]	−1.095	−1.670	−1.450	−0.010

[a] From ref. 8 and converted to values *vs.* SCE. [b] This work; [c] Scan rate 100 mV s^{-1}. [d] Scan rate 80 mV s^{-1}.

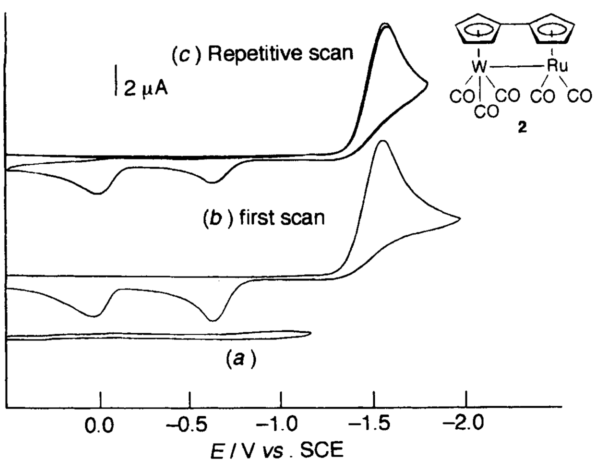


Fig. 1 Cyclic voltammogram of a 2.85 × 10^{-5} mol dm^{-3} solution in tetrahydrofuran (THF) of complex **2** (0.1 mol dm^{-3} $Bu^n{}_4NBF_4$ at a Pt cathode; scan rate 0.4 V s^{-1}; room temp.). (*a*) switching potential before the reduction wave (E_{sp} = −1.2 V); (*b*) switching potential before the reduction wave (E_{sp} = −2.0 V); (*c*) continuous scan with E_{sp} = −1.8 V. All potentials are relative to the standard calomel electrode (SCE).

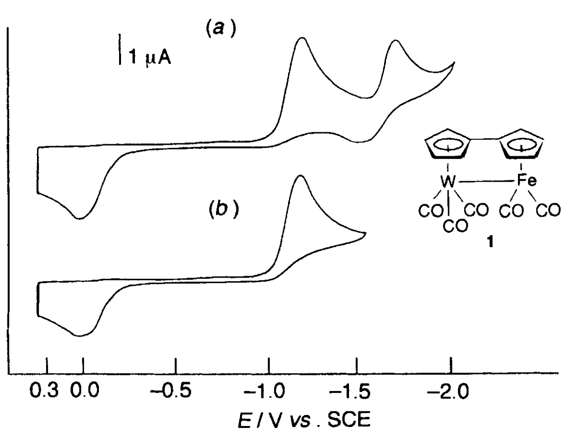
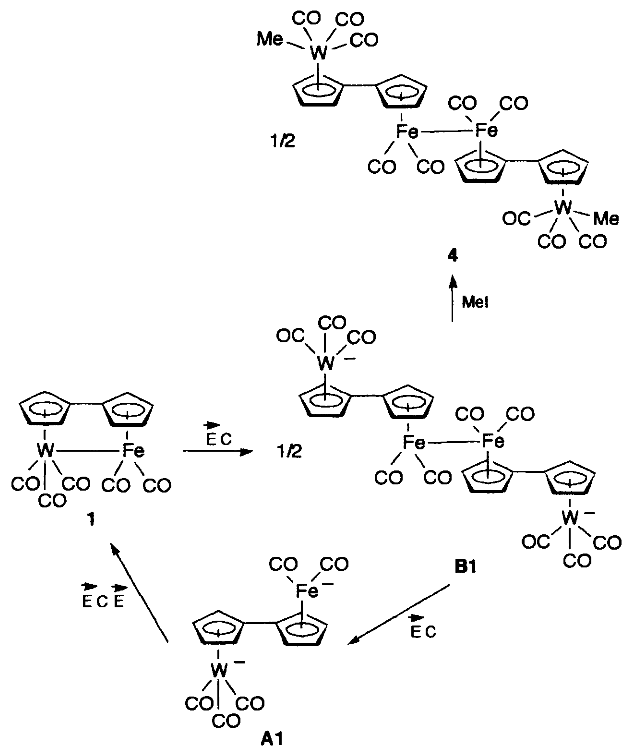


Fig. 2 Cyclic voltammograms of a 1.85 × 10^{-5} mol dm^{-3} THF solution of complex **1** (0.1 mol dm^{-3} $Bu^n{}_4NBF_4$ at a Pt cathode; scan rate 0.4 V s^{-1}; (room temp.). (*a*) Scan between 0.3 and −2.0 V: allowing the observation of two waves; (*b*) switching potential applied at −1.5 V, *i.e.* between the two reduction waves.

homodimeric fulvalene analogues. Although the thermodynamic $E°$ values are not accessible from the CVs owing to the complete chemical irreversibility of all the waves, the peak values E_p give an idea of the ease of the reductions, being recorded over the small range of sweep rates from 80 to 100 mV s^{-1}.

The variations of these E_p values with scan rates (V) give invaluable information on the electrochemical reversibilities.[10] All the variations of E_p *vs.* log v show straight lines with correlation coefficients between 0.93 and 0.99 and slopes around 60 ± 10 mV indicating slow heterogeneous electron transfer (first $\overrightarrow{E}$ in the $\overrightarrow{E}C$ process for **1** → and in the $\overrightarrow{E}C\overrightarrow{E}$ process for **2**). Only the second reduction wave of **1** has a $\Delta E_p/\Delta \log v$ = 22 mV with a correlation coefficient of 0.84, indicating a reversible (fast) heterogeneous electron transfer followed by a fast and irreversible chemical step.

Table 1 indicates that the W centre of **1** is reduced first to a radical anion which we assume dimerizes to the tetranuclear dianion **B1**. The latter is then reduced to the classical dianion **A1** which is directly reoxidized by an $\overrightarrow{E}C\overrightarrow{E}$ process to **1** (Scheme 2).

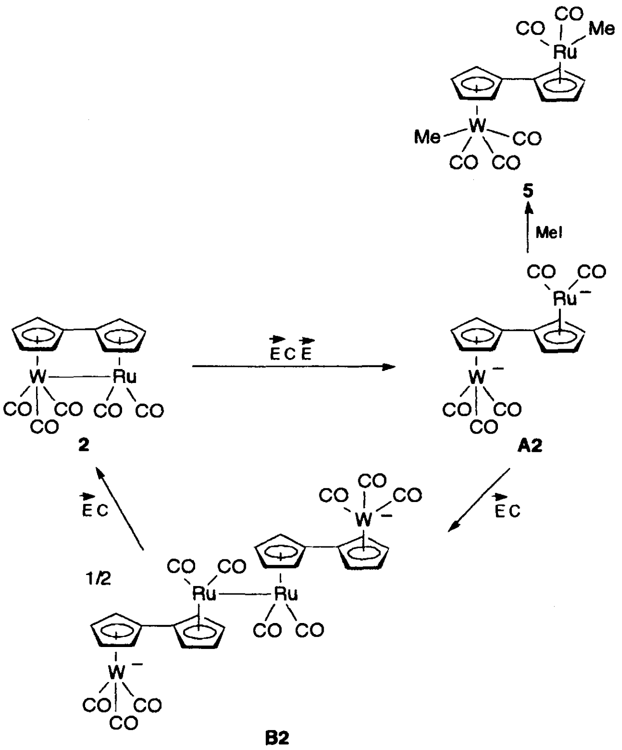


Scheme 2

In contrast **2** is reduced in a two-electron $\overrightarrow{E}C\overrightarrow{E}$ process to the dianion **A2**, the one-electron reoxidation of which gives the tetranuclear dianionic species **B2** (analogous to **B1**). The oxidation of the proposed intermediate **B2** could eventually give **2**, *via* an unstable oligomeric intermediate (Scheme 3).

This electrochemical information has synthetic implications, and we have used the electron-reservoir complex $[Fe^I(C_5H_5)(C_6Me_6)]$ **3** to check the mechanisms of Schemes 2 and 3 since this synthon complex has an $E°$ value around −1.55 V *vs.* SCE in aprotic solvents. This potential is sufficient to expect an exergonic (thus fast) electron transfer to the complexes $[WM(fulvalene)(CO)_5]$ to take place, whereas cobaltocene ($E°$ = − 0.9 V *vs.* SCE) is too weak a reducing agent.[2] The one-electron reduction of **1** using **3** in tetrahydrofuran (THF) specifically reduces the W centre subsequent to cleavage of the W–Fe bond (see Table 1). The reaction at 20 °C is fast and provides a red dimer of the radical anion which was quenched using MeI. The deep red complex **4** obtained (see Scheme 2) slowly decomposes under N_2 at 20 °C over several days. Its 300 MHz ^1H NMR spectrum in $[^2H_8]THF$ shows four triplets due to the fulvalene ligands at δ 5.92, 5.57, 5.14 and 4.77 (^3J = 2.1–2.2 Hz) and a singlet at high field (δ 0.26) as expected for the $W–CH_3$ protons. The relative intensity of the fulvalene and CH_3 signals is 8 : 3. These features indicate a symmetrical tetranuclear structure **4**. Reduction of **2** proceeds to completion using two equivalents of **3** and directly gives the thermally stable dianion which was quenched once again using MeI to yield the thermally stable yellow dimethyl complex **5** (see Scheme 3). Its 300 MHz ^1H NMR spectrum in $[^2H_8]THF$ shows four triplets at δ 5.79, 5.59, 5.47 and 5.44 (^3J = 2.1–2.2 Hz) and two distinct singlets at high field [δ 0.31 (W) and 0.25 (Ru)] as expected for the two methyl groups. The fulvalene to methyl intensity ratio is now 8 : 6. The molecular ion peak (M^+, *m/z* 584) is observed in the mass spectrum of **5**. In both reductions of **1** and **2**, the only other product observed in the NMR spectrum of the reaction mixtures is the $[Fe(C_5H_5)(C_6Me_6)]^+$ salt.

The electrochemical mechanisms are thus supported by the synthetic data.



Scheme 3

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