The Novel Electrochemistry of the Decaosmium Cluster $[Os_{10}C(CO)_{24}]^{2-}$

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Electrochemical studies of $[Os_{10}C(CO)_{24}]^{2-}$ have allowed five oxidation states to be characterized; the two-electron reduction of $[Os_{10}C(CO)_{24}]^{2-}$ has been resolved at −50 °C into a reversible process followed by an irreversible wave associated with a structural change.

Oxidized and reduced states of large metal carbonyl clusters are of increasing interest. Previous electrochemical studies of metal clusters have shown that changes in structure are often associated with redox processes,[1—5] but in most cases the cyclic voltammograms of these species show reversible oxidation or reduction processes (as seen in $[Fe_4S_4Cp_4]^{4+/3+/2+/+/0}$ and $[Fe_4S_4(CO)_4]^{3+/2+/+/0}$).[4—6] This means that it is difficult to correlate the structural changes with the observed electrochemistry, because if the change in structure is fast and reversible, then electrochemically reversible redox processes will be observed.[7] In these cases a low activation energy for a change in the geometry of the cluster core is implied and it has been suggested that some of these clusters {*e.g.* $[Au_9(PPh_3)_8]^{3+}$} may be in a continual fluxional state in solution.[3] However evidence[8] is mounting that for some osmium clusters the activation energy for structural change is much higher. This is reflected in slower heterogeneous charge-transfer kinetics and the observation of electrochemically irreversible redox processes, as reported[2] for $Os_6(CO)_{18}$ [reaction (1)], rather than reversible electrochemical features.

$$Os_6(CO)_{18} + 2e^- \rightarrow [Os_6(CO)_{18}]^{2-} \qquad (1)$$

In this communication we report electrochemical and chemical evidence that the two-electron reduction of an osmium cluster $[Os_{10}C(CO)_{24}]^{2-}$ (**1**) proceeds in two stages: the first electron is added rapidly and reversibly, while the addition of the second electron is electrochemically irreversible and associated with a structural change. Although some evidence for this conclusion has been previously reported for a gold cluster,[3] we believe this work to be the first direct observation of the splitting of a two-electron reduction of a cluster into two separate redox processes with very different electrochemical properties.

We have recently reported upon the electrochemical oxidation of $[Os_{10}C(CO)_{24}]^{2-}$ (**1**) to generate $[Os_{10}C(CO)_{24}]^-$ and $[Os_{10}C(CO)_{24}]$.[9] Chemical reduction of (**1**)[10] by the rapid addition of an excess of sodium benzylphenyl ketyl solution in tetrahydrofuran (THF) generated $[Os_{10}C(CO)_{24}]^{4-}$ (**2**). The i.r. spectrum of (**2**) (Table 1) is very similar to that of (**1**) except that the peaks are about 40 cm^{-1} lower in frequency and broadened.† The poorly resolved splitting of the i.r. peaks is consistent with a decrease in symmetry from the T_d point group of (**1**). Exposure of (**2**) to air regenerated (**1**) quantitatively. In contrast the slow addition (over 15 min) of 1 to 2 equiv. of sodium benzylphenyl ketyl to a solution of (**1**) in THF gave a third species with an i.r. spectrum intermediate (Table 1) between those of (**1**) and (**2**). This was $[Os_{10}C(CO)_{24}]^{3-}$ (**3**), and in the presence of an excess of sodium benzylphenyl ketyl it slowly generated (**2**). In the absence of an excess of reducing agent (**1**) was slowly re-formed, and this observation is consistent with the slow disproportionation of (**3**) to a mixture of (**1**) and (**2**), with the

Table 1. I.r. data (solvent THF).

Species		ν/cm^{-1}
$[Os_{10}C(CO)_{24}]^{4-}$	(**2**)	1988, 1941
$[Os_{10}C(CO)_{24}]^{3-}$	(**3**)	2010, 1966
$[Os_{10}C(CO)_{24}]^{2-}$	(**1**)	2033, 1986
$[Os_{10}C(CO)_{24}]^-$		2054, 2010[a]
$[Os_{10}C(CO)_{24}]$		2078, 2030[a]

[a] From ref. 9.

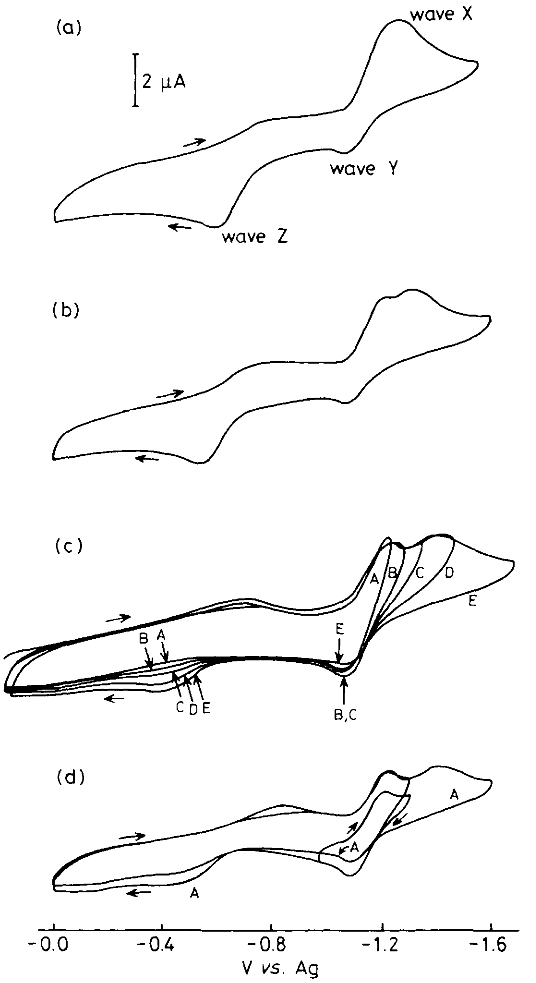

Figure 1. The cyclic voltammogram of $[Os_{10}C(CO)_{24}]^{2}$ (**1**) in THF–0.1 M TBAF, showing the effect of temperature on the shape of wave X: (a) −5 °C, (b) −25 °C, (c) −35 °C with a range of switching potentials, (d) −50 °C. All scan rates are 100 mV s^{-1}, and the voltammograms are recorded against an Ag wire pseudoreference (see ref. 9).

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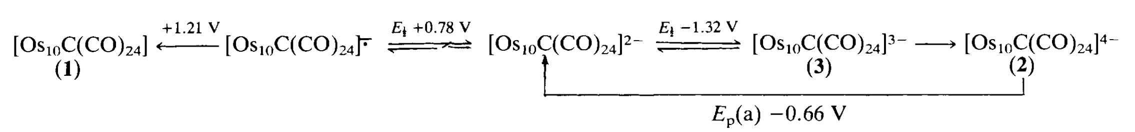
† For i.r. spectra obtained in absorbance mode in CH_2Cl_2 the full peak width at half maximum intensity (f.w.h.m.) for the high frequency peak of (**2**) was 20 cm^{-1}, and for the lower frequency peak was 15 cm^{-1}. For (**1**), (**3**), and the monoanion the f.w.h.m. value for both absorptions was consistently 9—10 cm^{-1}. The small broadening of the i.r. absorptions for (**2**) suggests that the associated structural change is very minor and not the expected edge-breaking reaction that might be predicted on the basis of electron-counting rules.



$$\underset{(1)}{[Os_{10}C(CO)_{24}]} \xleftarrow{+1.21\ V} [Os_{10}C(CO)_{24}]^{-} \overset{E_{\frac{1}{2}}\ +0.78\ V}{\rightleftharpoons} [Os_{10}C(CO)_{24}]^{2-} \overset{E_{\frac{1}{2}}\ -1.32\ V}{\rightleftharpoons} \underset{(3)}{[Os_{10}C(CO)_{24}]^{3-}} \longrightarrow \underset{(2)}{[Os_{10}C(CO)_{24}]^{4-}}$$

$E_p(a)$ −0.66 V

Scheme 1. The electrochemistry of $[Os_{10}C(CO)_{24}]^{2-}$. Potentials are quoted against an Ag/AgCl reference electrode in CH_2Cl_2–0.1M TBAF at a scan rate of 100 mV s^{-1}.

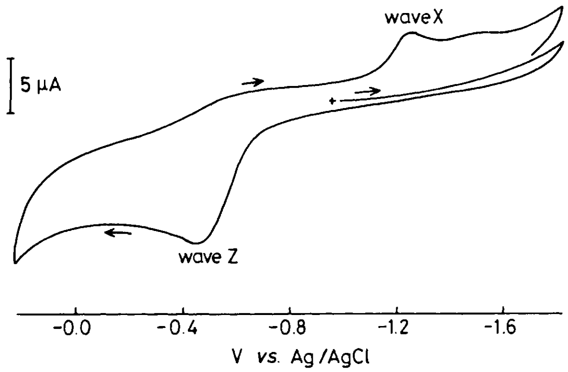


Figure 2. The cyclic voltammogram of $[Os_{10}C(CO)_{24}]^{4-}$ (**2**) generated in 0.1M TBAF–MeCN by electrochemical reduction of (**1**) (scan rate 100 mV s^{-1}). Note that wave X is only observed after scanning through wave Z.

latter being oxidized by trace oxygen present under the experimental conditions.

In the cyclic voltammogram of (**1**)[9] in THF or CH_2Cl_2 at a Pt electrode [Figure 1(a)] an electrochemically irreversible reduction at about −1.4 V (wave X) was followed by a weak corresponding oxidation wave (Y, ΔE_p < 100 mV) and a further oxidation wave (Z) at more positive potentials.‡ Wave Z was broad and only observed after scanning through wave X. Controlled potential reduction of (**1**) in THF or MeCN at approximately −1.5 V required 2.0 ± 0.2 electrons per molecule of (**1**). This product (**2**) is spectroscopically identical with that obtained by chemical reduction of (**1**). The cyclic voltammograms of solutions of (**2**) (Figure 2) show a broad oxidation of high peak current at the potential of wave Z before reduction and are consistent with the oxidation of (**2**) to (**1**). Wave X is now very weak and is only observed after scanning through the intense wave Z, and wave Y is completely absent. Samples of (**2**) are easily oxidized back to (**1**) either chemically (air) or electrochemically in close to 100% yield. In addition, i.r. and cyclic voltammetric studies of such regenerated solutions of (**1**) showed no evidence for the formation of any other chemical species in these solutions, demonstrating that the interconversion of (**1**) and (**2**) is chemically reversible. The presence of a structural change upon reduction of (**1**) by two electrons is suggested by (a) the linked nature of waves X and Z along with the differences of the cyclic voltammograms of (**1**) and (**2**), and (b) the broadening of the i.r. peaks for (**2**).†

On cooling a solution of (**1**) in THF–0.1M tetrabutylammonium fluoride (TBAF) (Figure 1 (b—d)], wave X gradually broadened and the peak current decreased. By −25 °C the broad wave was showing evidence of splitting into a wave that was quasi-reversible with wave Y and a broad, well defined irreversible wave (X′) that moved steadily to more negative potentials as the solution was cooled. These observations are consistent with a reversible one-electron process (linked with wave Y) followed by a kinetically slow irreversible one-electron wave. At −50 °C waves X and Y were of the same intensity and showed a ΔE_p value of about 130 mV.§ Increasing the temperature causes the same changes in the form of the cyclic voltammogram to occur in reverse.

At −35 °C, increasing the switching potential through wave X caused a steady increase in the intensity of wave Y, but there was no sign of wave Z. However as soon as reduction into wave X′ occurred then wave Z started to appear and wave Y began to diminish. At more negative switching potentials, wave Z continued to increase in intensity at the expense of wave Y. This demonstrates that wave Y is linked to wave X, while wave Z is due to a product of wave X′.

Solutions containing 0.3M TBAF–THF showed better separation of the waves for a given temperature. Thus at −35 °C wave X′ was well separated from waves X and Y, which now showed the characteristics of a reversible electrochemical process (ΔE_p = 60—80 mV), suggesting that the addition of the first electron to the cluster is close to diffusion-controlled at these scan rates. The separation of waves X′ and Z was analysed as a function of scan rate using the methods of Nicholson,[11,12] and suggested a heterogeneous charge-transfer constant (k_s) for the addition of the second electron to the cluster of about 4×10^{-6} cm s^{-1}.

In conclusion, the addition of the first electron to (**1**) is fast and reversible generating the trianion (**3**) with no structural change. The addition of the second electron in contrast shows slow heterogeneous charge-transfer (giving broad waves for processes X′ and Z) because it is concomitant with a structural change. At room temperature the potential for the second electron addition is positive of that of the first reduction, so an approximately two-electron process is observed. This is also consistent with the disproportionation of (**3**) at room temperature. On cooling, the second wave moves to more negative potentials causing the splitting of the two-electron wave.

It should be noted that $[Os_{10}C(CO)_{24}]^{2-}$ is the only osmium cluster to date and one of few clusters of any type to have been characterized in five oxidation states[9] (Table 1). The sequence $[Os_{10}C(CO)_{24}]^{0/-/2-/3-/4-}$ contains three diamagnetic species and two radical species. The impressive range of redox states for this cluster (Scheme 1) testifies to the great stability of the '$Os_{10}C(CO)_{24}$' core.

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‡ Unless otherwise stated all solutions used for electrochemical experiments were 0.1M in electrolyte (tetrabutylammonium tetrafluoroborate) (TBAF) and potentials are quoted against a Ag/AgCl reference (the $Fc^{+/0}$ couple was +0.56 V in CH_2Cl_2 and +0.44 V in THF on this scale) except for the low temperature experiments where an Ag wire pseudoreference was used instead. Where the pseudoreference was used, ferrocene was added as an internal standard, and under these conditions the $Fc^{+/0}$ couple was +0.64 V and independent of temperature. All potentials are uncorrected for solution resistance and junction potentials. Typical scan rates used were 100 or 200 mV s^{-1}.

§ The high ΔE_p value for this process was due to uncompensated solution resistance and was also observed for the reversible oxidation of the ferrocene used as an internal standard. These effects are due to the high resistance of dilute solutions of electrolyte in THF.

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