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Registry No. $[Na(C_4H_8O)_6][Nd(\eta^5\text{-}C_4H_7)_3(\mu\text{-}Cl)Nd(\eta^5\text{-}C_9H_7)_3]$, 112630-30-5; $NdCl_3$, 10024-93-8; NaC_6H_7, 23181-84-2.

Supplementary Material Available: Tables of crystal data, general temperature factor expressions, positional parameters, bond distances, bond angles, and least squares planes (10 pages); a listing of structure factor amplitudes (18 pages). Ordering information is given on any current masthead page.

Redox Chemistry of the Cluster $[Os_{10}C(CO)_{24}]^{2-}$

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The dianion $[Os_{10}C(CO)_{24}]^{2-}$ (1) is oxidized at a hanging drop mercury electrode (HDME) in a variety of media to produce $[Os_{20}(C)_2(CO)_{48}Hg_2]^{2-}$ (2), which on standing ultimately yields the known $[Os_{20}Hg(C)_2(CO)_{48}]^{2-}$ (3). The dianion 1 is readily reduced electrochemically (at wave A in the cyclic voltammogram) by two electrons to yield the tetraanion $[Os_{10}C(CO)_{24}]^{4-}$ (5). This reduction was studied at a variety of electrodes and in different media and was found to be associated with an oxidation at more positive potentials (wave C). Electrochemical studies of 5 showed that 1 and 5 could be readily interconverted in close to 100% yield showing that the two redox processes were chemically reversible. From a comparison of the electrochemical and IR properties of 1 and 5 it was concluded that the two-electron reduction of 1 generated 5 with an associated minor change in structure, a process that was reversed upon oxidizing at wave C. When a solution of 1 is cooled, the two-electron wave (wave A) split into a quasi-reversible one-electron process and an irreversible wave which moved to more negative potentials as the temperature was reduced. The broad wave was linked to the oxidative feature (wave C) and demonstrated that the structural change occurs on the addition of the second electron to 1. The quasi-reversible electrochemical process was associated with the formation of the trianion $[Os_{10}C(CO)_{24}]^{3-}$ (4) which could be independently synthesized by the slow chemical reduction of 1. As suggested by the electrochemical results, samples of 4 disproportionated at room temperature and hence could not be further characterized. The species 2–5 have been prepared by independent chemical methods.

Introduction

Oxidized and reduced states of large metal carbonyl clusters are of increasing interest. This is due in part to their higher reactivity and also to the possible analogy between the binding of ligands to a metal cluster and the binding of ligands to a metal surface.[1,2] The chemistry and reactivity of high nuclearity osmium clusters has been previously reported,[3] but little information on the redox chemistry of these species and the related high nuclearity nickel, cobalt, and rhodium species is available.[4] However, of the larger clusters that have been studied by electrochemical techniques it has been reported that the addition or removal of electrons is often associated with changes in structure. Well-defined examples include $[FeCpS]_4$ and $[FeCp(CO)]_4$ which both show several reversible one-electron steps, each associated with a small change in the structure of the cluster.[5,6] In a similar way $[Au_9(PPh_3)_8]^{3+}$ shows two reversible one-electron processes and a structural change,[7] but in all these cases the electrochemically reversible nature of the waves in the cyclic voltammogram (CV) show that the structural changes are fast and reversible.[8] With osmium carbonyl clusters evidence is mounting[9,10] that the stronger Os–Os bonds lead to higher activation energies for structural changes generating electrochemically irreversible features in the CV. The reductive electrochemistry of 1 shows two linked irreversible electrochemical waves. Such features are usually associated with slow electron-transfer caused by a change in structure of the cluster. Further studies showed that the two-electron reduction of 1 could be split into two one-electron processes. The addition of the first electron was found to be fast and electrochemically reversible, but the addition of the second electron is slower and appeared to be associated with the expected change in cluster structure. Evidence that the structural change in a cluster occurred upon the addition of the second electron has been previously reported,[7] but this is the first time that the

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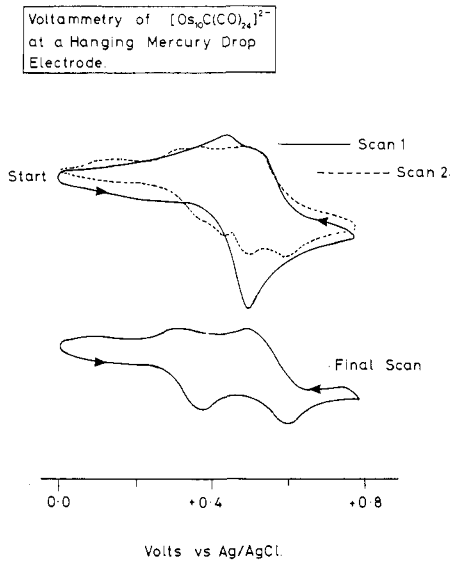

Figure 1. Cyclic voltammogram of ~5 × 10^{-3} mol·dm^{-3} $[N(PPh_3)_2]_2[Os_{10}C(CO)_{24}]$ (1) at a hanging drop mercury electrode in CH_2Cl_2–0.1 M TBAF (scan rate = 200 mV/s).

process has been directly observed by electrochemical means. The electrochemistry of 1 at positive potentials at a Pt electrode has been described in our previous paper,[11] along with the characterization of the oxidation products.

In this paper we wish to report the oxidation of $[Os_{10}C(CO)_{24}]^{2-}$ (1) in a variety of media at a hanging drop mercury electrode (HDME) to generate the previously reported $[Os_{20}Hg(C)_2(CO)_{48}]^{2-}$ (3)[12] and the reductive electrochemistry of 1 in different media to form $[Os_{10}C(CO)_{24}]^{4-}$ (5). Clusters 2–5 have also been prepared by classical chemical procedures.

Results and Discussion

Whereas the oxidation at a Pt electrode of 1 gives only a single reversible oxidation at potentials below +1.0 V,[11] the electrochemistry of this species at a HDME is much more involved (Figure 1). On the first scan a single intense wave is observed at about +0.5 V, and on the second and subsequent scans this wave gradually decreases until a steady-state voltammogram is obtained after about five scans. This new voltammogram shows two quasi-reversible oxidations at $E_{1/2}$ = +0.40 and +0.62 V indicating that a new species has been generated on the mercury's surface.

Controlled potential electrolysis at +0.8 V of 1 in CH_2Cl_2 at a Hg pool yields a new dianion (2) which exhibits an IR spectrum almost identical with that of the recently reported $[N(PPh_3)_2][Os_{10}C(CO)_{24}HgCl]$.[12] In this latter compound the HgCl moiety is considered to be isolobal with the structurally characterized $[N(PPh_3)_2][Os_{10}C(CO)_{24}AuBr]$,[12] where the AuBr ligand is μ_3 face capping. On the basis of this (and mass spectral data) and the fact that the IR and reactivity of 2 are similar to those of $[Os_{10}C(CO)_{24}HgCl]^-$,[12] suggesting a similarity of structure between this compound and 2, 2 was provisionally formulated as $[Os_{20}(C)_2(CO)_{48}Hg_2]^{2-}$ with the structure given in Figure 2. We propose each Os_{10} unit to be μ_s face capped by a Hg atom which is then linked to the corresponding Hg atom on the other unit forming a $Hg_2{}^{2+}$ bridge between the two osmium clusters. Other examples of dimercury-linked clusters have been characterized and reported in the literature, e.g., $Hg_2[Pt_3(\mu_2\text{-}CO)_3PR_3]_2$.[13] Similar electrochemical behavior is observed in THF and 1,2-dimethoxyethane.

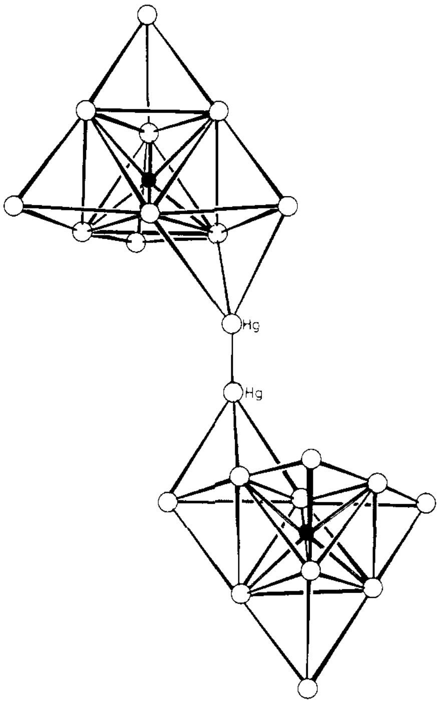

Figure 2. Proposed structure for $[Os_{20}Hg_2(C)_2(CO)_{48}]^{2-}$ (2).

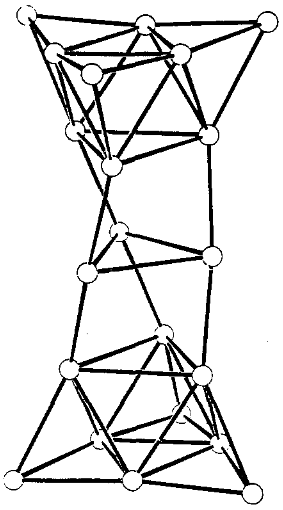

Figure 3. The metal core geometry of $[Os_{20}Hg(C)_2(CO)_{48}]^{2-}$ (3) (from ref 12).

The chemical oxidation of 1 with $AgBF_4$ in CH_2Cl_2 in the presence of excess Hg also yields 2 after ca. 2 h. Solutions of 2 in CH_2Cl_2 (excess Hg removed by filtration) on standing under nitrogen slowly extrude metallic mercury with the formation of the recently characterized *eicosa*-osmium species $[Os_{20}Hg(C)_2(CO)_{48}]^{2-}$ (3).[12] Recent X-ray results[12] show that in 3 the Hg atom has become part of the 6:3:3:3:6 close-packed metal array (Figure 3).

Mercury is known to interact strongly with many organometallic complexes[13,14] and to speed up the kinetics of some electrochemical reactions.[15] It is possible that a

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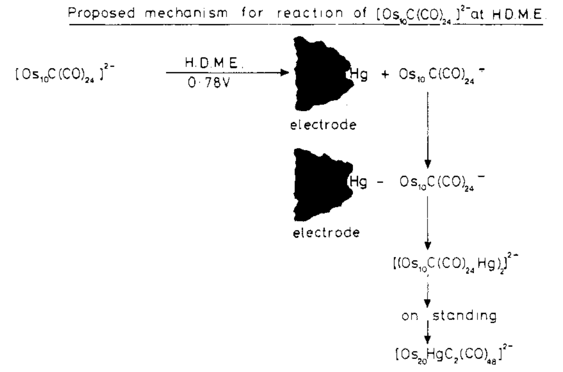

Figure 4. Proposed mechanism of the interaction of $[Os_{10}C(CO)_{24}]^{2-}$ (1) at a hanging mercury drop electrode.

Table I

solv	electrode	wave A E_p(c), V	wave C E_p(a), V	ΔE_p,[a] mV
CH_2Cl_2	Pt	−1.32	−0.66	660
	Au	−1.30	−0.65	650
	Hg	−1.26	−0.80	460
THF	Pt	−1.43	−0.92	510
	Au	−1.38	−0.88	500
	Hg	−1.34	−0.98	360
CH_3CN	Pt	−1.26	−0.44	820
	Au	−1.24	−0.5[b]	740
	Hg	−1.20	−0.74	460

[a] $\Delta E_p = E_p(c) - E_p(a)$. [b] Wave C very poorly defined at switching potentials 300 mV cathodic of wave A. Hence this E_p(a) value and the appropriate ΔE_p value are only approximate.

similar interaction in this case may lead to the incorporation of mercury into an oxidized form of 1, forming 2 by dimerization which then slowly undergoes a rearrangement to give 3 as the final product (Figures 3 and 4). Evidence for the strong interaction between 1 and Hg electrode is found in the reductive electrochemistry of 1 (see below).

The reductive electrochemistry of 1 was studied in three solvents (CH_2Cl_2, CH_3CN, and THF) and at three different electrodes (Hg, Pt, and Au). In the CV of 1 (Figure 5) an electrochemically irreversible reduction at about −1.2 V was consistently observed as a well-formed wave (wave A in Figure 5 and Table I). At Pt and Au electrodes and in all the solvents studied this two-electron reduction (see below) showed a weak corresponding oxidation wave (wave B, $\Delta E_p < 100$ mV) followed by a further oxidation wave (wave C) at more positive potentials. The potential of wave A varied only slightly (usually <60 mV) with the electrode used for a given solvent. The variation of potential with solvent was consistent with the formation of a more highly charged species on reduction (Table I); thus this highly charged species was most effectively solvated by CH_3CN and least solvated by THF, and this is reflected in the reduction potentials. Wave C was observed at a potential that was very sensitive to both the electrode material and the solvent used (range −0.34 to −0.98 V) and was only observed after scanning through wave A (Figure 5C).

Controlled potential reduction of a red-brown solution of 1 in THF or CH_3CN (0.1 M TBAF) at a potential aproximately 200 mV cathodic of the potential of wave A is accompanied by the darkening of the solution and the absorption of 2.0 ± 0.2 electrons per molecule of 1. The new species $[Os_{10}C(CO)_{24}]^{4-}$ (5) is spectrally identical with that obtained by chemical reduction of 1 and is extremely air sensitive (reverting to 1 by a two-electron oxidation).

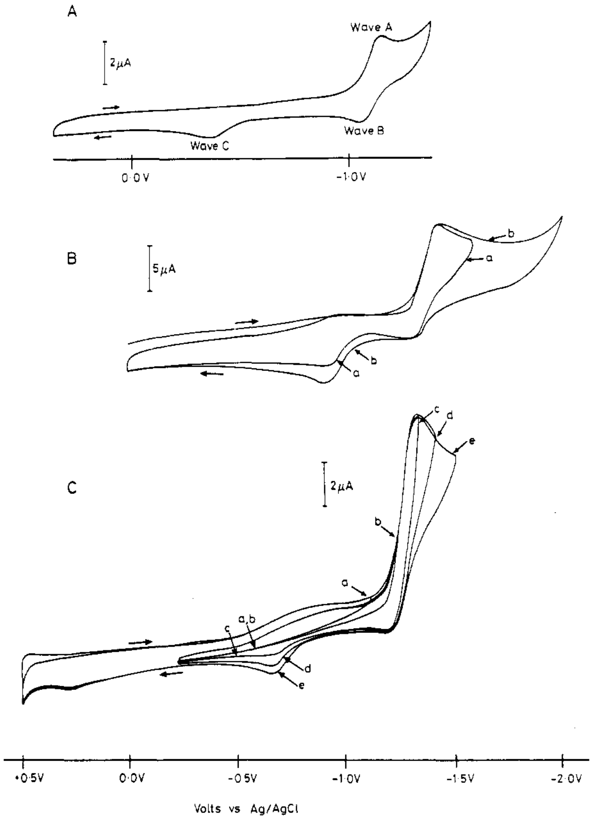

Figure 5. Cyclic voltammograms of 1 in various solvents (0.1 M TBAF as the electrolyte): (A) in CH_3CN; (B) in THF with switching potentials at −1.6 and −2.0 V; (C) in CH_2Cl_2 showing that wave C is only generated after scanning through wave A. (scane rates = 100 $mV\cdot s^{-1}$).

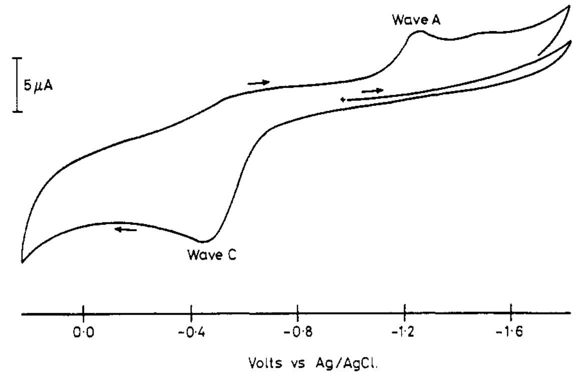

Figure 6. Cyclic voltammogram of $[Os_{10}C(CO)_{24}]^{4-}$ (5) generated in 0.1 M TBAF-CH_3CN by the electrochemical reduction of 1 (scan rate = 100 $mV\cdot s^{-1}$). In this case wave A is only observed after scanning through wave C.

The CV of solutions of 5 (Figure 6) shows a very intense, broad oxidation at the potential of wave C before reduction. This is consistent with the oxidation of 5 to 1 at wave C although in both solvents this wave shows some non-Nernstien structure, suggesting slow charge-transfer characteristics for this oxidative process. Wave A is now very weak and is only observed after scanning through the intense wave C and wave B is completely absent. Reduction of 1 to 5 followed by oxidation at a potential positive to that of wave C regenerated 1 in quantitative yield as judged by the clean IR spectrum and CV of the product solution. This confirmed the chemical reversibility of the redox processes involved in the interconversion of 1 and 5 and showed that other products were not generated in these reactions. Hence waves A and C were linked irreversible redox processes separated by some hundreds

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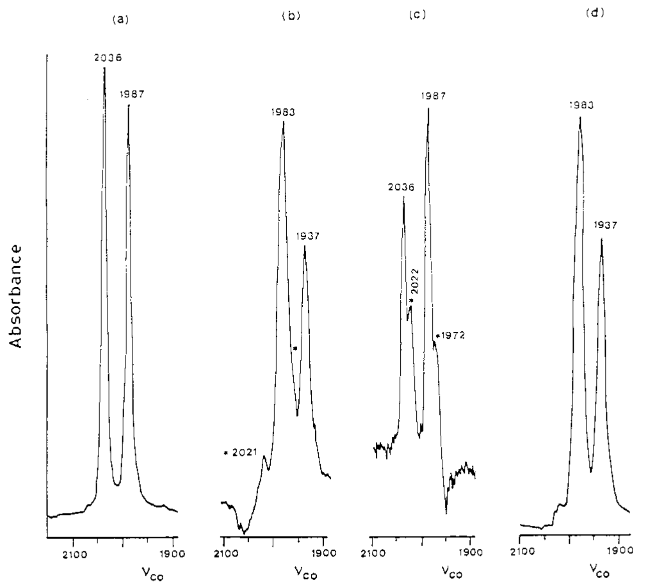

Figure 7. See ref 17. IR spectra obtained from the electrochemical reduction and oxidation of $[Os_{10}C(CO)_{24}]^{2-}$ (**1**) in a thin-layer IR transparent electrochemical cell. All spectra are in CH_2Cl_2–0.5 M TBAF. Features marked with an asterisk in spectra b and c are due to $[Os_{10}C(CO)_{24}]^{3-}$ (**4**) generated as an intermediate at low concentration during the reduction of **1** to **5**. (a) Spectrum of $[Os_{10}C(CO)_{24}]^{2-}$ (**1**). (b) Spectrum of product solution generated by electrolyzing **1** at −1.2 V for 5 min and then absorbance subtracting out the spectrum of the residual **1**. Principle absorptions are due to **5**. (c) Spectrum of the product solution after reducing >95% of the original **1** and then absorbance subtracting out the spectrum of the electrochemically generated **5**. Principle absorptions are due to residual **1**. (d) Spectrum of $[Os_{10}C(CO)_{24}]^{4-}$ (**5**) generated by the exhaustive electrolysis of a solution of **1** at −1.6 V for 10 min.

of millivolts. This is consistent with a two-electron redox process at an intermediate potential complicated by slow heterogeneous charge transfer[16] in a system analagous to that observed for the two-electron reduction of $Os_6(CO)_{18}$.[9]

In CH_2Cl_2, using $TEA^+ClO_4^-$ as an electrolyte, the reduced product precipitated out as a black microcrystalline solid, which was characterized by microanalysis, IR, and NMR and shown to be the mixed salt $[TEA]_2[PPN]_2$-$[Os_{10}C(CO)_{24}]$ (**5**).

Chemical reductions of clusters have been achieved by using Na/benzyl ketyl solution.[18] We found that using an excess of this reagent in THF rapidly reduced **1** to **5**. In both chemical and electrochemical reductions the IR shows little change of form. Reduction causes the two IR absorptions of **1** (at 2033 and 1986 cm^{-1}) to move to lower frequencies (1985 and 1938 cm^{-1} for **5**) with some broadening of the peaks. The change in IR was conveniently studied by the electrochemical reduction of **1** in THF or CH_2Cl_2 in a thin-layer IR transparent electrochemical cell[17] (Figure 7). A comparison of the full peak width at half-maximum intensity for the two absorptions of **1** and **5** (Figure 7, parts a and d) shows that for the oxidized cluster this width was consistently 9–11 cm^{-1} for both absorptions while for **5** this increased to 15 cm^{-1} for the low-frequency absorption and 20 cm^{-1} with some assymmetry for the high-frequency absorption. These results are consistent with a fine splitting of these two principal absorptions which are poorly resolved due to the very polar media required for the electrochemical experiment. Oxidation of chemically reduced solutions by moist air regenerated the original IR spectrum including the original narrow peaks. Solutions of chemically prepared samples of $[Os_{10}C(CO)_{24}]^{3-}$ (**4**) showed peak widths similar to those observed for **1** suggesting that no splitting of the principal absorptions occurred for this species. The two absorptions in the IR of **1** are characteristic of a tetrahedrally symmetric cluster, and the broadening of these absorptions upon reduction to **5** is consistent with a small structural change in the cluster that does not destroy any of the major symmetry elements. This minor structural change probably involves an expansion of one of the tetrahedral caps and certainly does not involve any edge breaking or the incorporation of bridging ligands. The IR results also show that the observed electrochemistry cannot be explained by the incorporation of solvent into the cluster upon reduction and the dissociation of this solvent molecule when the cluster is reoxidized. If the reduced species contained a coordinated solvent molecule, then the original tetrahedral symmetry of the cluster would be reduced and a complex multiline IR spectrum would be obtained.

Under conditions where wave C is observed, it is found that altering the switching potentials has a profound effect on the relative intensities of waves B and C. Although the relative intensities of waves B and C are sensitive to the solvent used and the nature of the electrodes, it is generally observed that with switching potentials that are less than 200 mV cathodic of the peak potential of wave A then wave B is well-defined. However, when the switching potential is increased, wave B gradually loses definition while wave C increases in peak current (Figure 5B). Reductive sweeps in THF allow a further multielectron process to be detected with $E_p = -2.5$ V. Sweeping into this reductive feature causes wave B to dissappear while wave C is strongly enhanced. These results taken with the results for the controlled potential electrolyses suggest that the addition of the second electron to **1** may occur on a slower time scale than the addition of the first electron.

Clarification of these results was obtained by the use of low-temperature cyclic voltammetry. CV's of a solution of **1** at room temperature in THF showed a single irreversible reduction (wave A) with a weak return wave (B) at a potential about 100 mV anodic of that for wave A. Comparison of the peak current of A with that of the known one-electron process[11] at +0.7 V ($[Os_{10}C(CO)_{24}]^{-/2-}$) suggests that wave A has an apparent electron stoichiometry ("*n* value") of about 1.7. This is consistent with a reversible one-electron process (linked with wave B) superimposed upon a kinetically slow (hence apparent *n* is less than 1) irreversible reduction process (call it A′). As the temperature is lowered (Figure 8), the $n = 1.7$ reduction becomes broader, and at −5 °C the apparent *n* has decreased to 1.2. By −15 °C the broad wave is showing signs of splitting, and by −25 °C a weak wave, apparently quasi-reversible with wave B, is followed by a well-defined but rather broad wave (wave A′). Decreasing the temperature further confirmed this separation as the broad wave steadily moved to more negative potentials until at −50 °C wave A and wave B were of similar peak current ($\Delta E_p = 130$ mV) consistent with a quasi-reversible one-electron reduction of **1** to give the trianion **4** with retention of the original structure. The gap between waves A and A′ is now 180 mV, and A′ is a well-defined broad wave with no return component (i.e., it is electrochemically irreversible). Increasing the temperature causes the same changes to occur in reverse.

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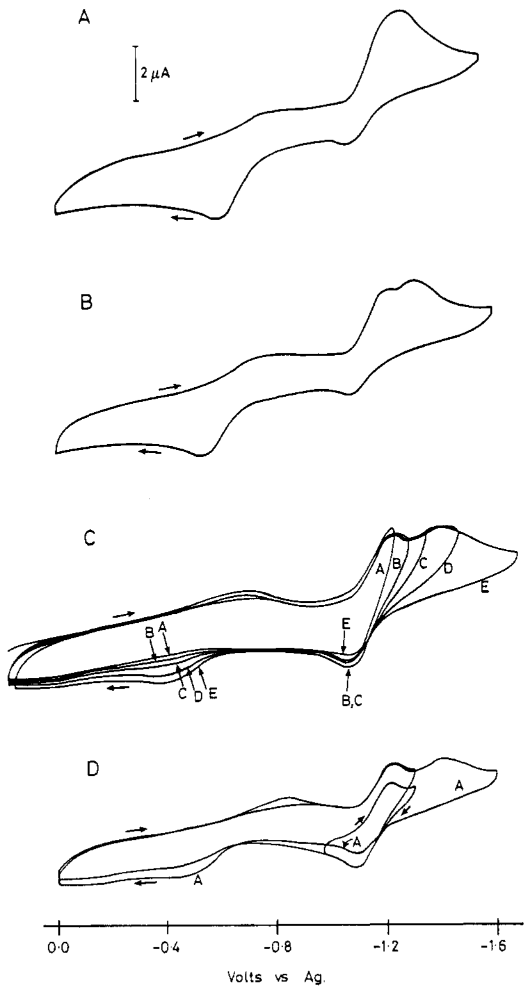
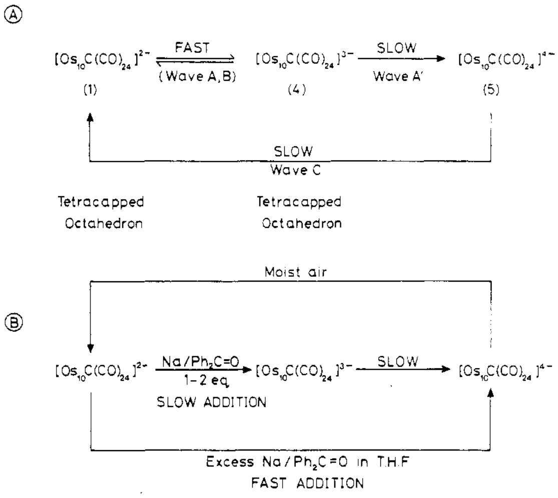


Figure 8. The effect of decreasing temperature on the shape of wave A in the cyclic voltammogram of 1 in THF–0.1 M TBAF: (A) −5 °C; (B) −25 °C; (C) −35 °C with a range of switching potentials; (D) −50 °C. All scan rates are 100 mV·s^{-1}, and the CV's were recorded against an Ag wire pseudoreference.

At −35 °C, gradually increasing the switching potential confirmed that wave A is quasi-reversible (or reversible)[19] with respect to wave B, while wave A′ is linked to wave C (Figure 8C). Hence switching the potential between waves A and A′ and scanning positively showed a strong wave B but no wave C. Increasing the switching potential out into wave A′ caused wave B to diminish and the previously missing wave C to reappear and increase steadily with the increasing switching potential. Hence the small structural change upon the reduction of the trianion 4 (also the second reduction of 1 appears to cause slow heterogeneous charge transfer and a substantial separation of waves A′ and C. It should be noted that in the low-temperature experiments wave C remained featureless and broad. It seems likely that the removal of the first electron from 5 causes a change in structure (back to the original structure of 1 which causes this first oxidation to be kinetically slow. This would generate 4 at a potential at which it would be rapidly oxidized; hence the removal of the second electron (to regenerate 1) would be fast and the two processes would not separate at low temperatures (Scheme I).

Scheme I



Electrochemical and chemical reduction of 1 showed some evidence that 4 could be formed as an intermediate during the preparation of 5. Although 5 was the usual product in the reduction of 1 by sodium benzyl ketyl, the careful addition of 1–2 equiv of this reagent to a sample of 1 generated 4 although this product disproportionated to a mixture of 1 and 5 at room temperature as suggested by the electrochemical results. A small proportion of 4 could also be detected during the electrochemical reduction of 1 to 5 (Figure 7, parts b and c).

At −35 °C in THF–0.3 M TBAF the Fc$^+$/Fc process showed a peak separation of close to 60 mV. Under these conditions waves A and B were separated by about 60 mV showing that the rate of the addition of the first electron was diffusion-controlled.[16] The separation of the two linked irreversible redox processes (waves A′ and C) increased with increasing scan rate, and this is consistent with the addition of the second electron being controlled by the rate of electron transfer across the electrode/solution interface rather than being affected by the rate of diffusion. Furthermore, it was possible to analyze the data according to the techniques of Nicholson[16,20] and to obtain an estimate of the heterogeneous rate constant for the addition of the second electron to the cluster of 4×10^{-6} cm s^{-1} at −35 °C. All these results are consistent with the first reduction of 1 being kinetically faster than the second reduction, with the rate of the second reduction (and hence the separation of waves A′ and C) being sensitive to temperature, electrode material, and the solvent.

In summary, the room-temperature data in Table I suggests a two-electron reduction of 1 followed by two oxidation processes (waves B and C). However, the behavior of this system with progressively increasing switching potential both at room temperature and at reduced temperature suggests that the apparent two-electron reduction process is two one-electron steps. The first step is fast and reversible, and the return component of this process is wave B. This process generates the trianion 4 whch can be obtained by the chemical reduction of 1 at room temperature and can be observed as an intermediate of low concentration during the electrochemical formation of 5. The addition of the second electron shows slow heterogeneous charge transfer and is associated with a small structural change. The product of this reduction is reoxidized at wave C. At room temperature the potential for the second electron addition is positive to that of the first reduction so an approximately two-electron process

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(19) The observed ΔE_p for this process of about 130 mV is substantially greater than the theoretical value for a reversible one-electron transfer (59 mV). This is due to uncompensated solution resistance (see Experimental Section), and a peak separation of close to 60 mV could be obtained in THF solutions containing higher concentrations (0.2 or 0.3 M) of electrolyte.

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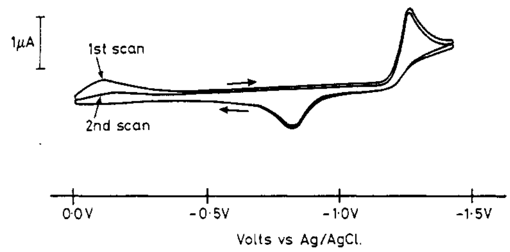

Figure 9. The electrochemistry of 1 at a HDME in CH_3CN–0.1 M TBAF (100 mV·s^{-1} scan rate). Upon scanning negatively from 0.0 V an extra quasi-reversible or irreversible reduction is observed before wave A is reached. This extra electrode process is probably linked with the complex electrochemistry seen for 1 at a mercury electrode at more positive potentials and may reflect some substitution of solvent molecules into the cluster.

is observed. On cooling the second wave moves to more negative potentials causing the splitting of the two-electron wave.

The potentials of waves A and C were almost identical at Au and Pt electrodes for a given solvent. This suggests that these electrodes are inert and do not participate in the mechanism (see above) of the reduction of 1.[21] However, the CV's at a HDME were very different in nature with wave A being completely irreversible with no oxidative component (wave B). A mercury electrode gave a much better defined oxidation wave (C) with smaller peak splittings (ΔE_p) than comparable scans with the solid electrodes (Figure 9). These results suggest that at a Hg electrode the rate of electron transfer and the nature of the reduced product is being strongly influenced by the interaction of the cluster with the surface of the mercury as has already been noted for oxidized forms of 1 (see above). Absorption on mercury has been found to dramatically alter the redox potentials of cobalt cluster compounds,[15] and it seems likely that a similar interaction may be occurring here.

We believe that this work demonstrates that electrochemical reduction of $[Os_{10}C(CO)_{24}]^{2-}$ occurs in two chemically reversible steps. The addition of the first electron is fast and reversible while the addition of the second electron is kinetically slow because of a small change in the structure of the cluster during this step. The surprising result is that such a minor change in structure is associated with such a substantial peak separation between the reduction and oxidation waves of this second reduction step. Other examples of this phenomenon are currently under investigation and will be reported in the near future.

Experimental Section

IR spectra were recorded on a Perkin-Elmer PE983 spectrophotometer. NMR (^1H) spectra were recorded on a Bruker WH 400 instrument, using CD_2Cl_2 as the internal calibrant. Mass spectra were recorded on a NEI MS12 mass spectrometer using tris(perfluoroheptyl)-1,3,5-triazine as calibrant, with the instrument in negative ion fast atom bombardment (FAB) mode, and using nitrobenzyl alcohol as the matrix.

Electrochemistry. Electrochemical experiments were performed by using a PAR Model 170 potentiostat with a standard three-electrode setup. Cyclic voltammograms (CV's) were obtained by using either (1) a hanging drop mercury electrode (HMDE-Metrohm EA 410) with a Pt wire auxiliary electrode or (2) a Pt bead electrode (Metrohm EA 235) with a similar auxiliary electrode. For controlled potential electrolysis the working electrode was either a Hg pool (7 cm^2 in area) or a Pt mesh (10 cm^2 area) with a smaller piece of Pt mesh as auxiliary electrode. The auxiliary electrode was separated from the working compartment by a porosity 4 sinter. The reference electrode was a Ag/AgCl(aq) electrode separated from the working solution by a cracked tip electrode containing CH_2Cl_2–0.1 M electrolyte as a salt bridge to ensure that no water leaked into the working solution.

For the CV experiments the effects of solution resistance were minimized by using 10^{-4}–10^{-3} M solutions of the sample and small electrodes so that peak currents were generally below 10 μA. All potentials are quoted vs. Ag/AgCl(aq) unless otherwise indicated and are uncompensated for solution resistance and the effects of liquid junction potentials. With use of this reference the $E_{1/2}$ value for ferrocene(1+)/ferrocene was +0.54 V in CH_2Cl_2, +0.66 V in THF, and +0.34 V in CH_3CN, in good agreement with literature values.[22]

Scan rates were varied between 20 and 500 mV·s^{-1} with 100 mV·s^{-1} as the standard scan rate.

Dichloromethane (laboratory grade) was repeatedly extracted with concentrated H_2SO_4 until the acid remained colorless. The CH_2Cl_2 was then washed with $NaHCO_3$ solution and water before drying over anhydrous Na_2SO_4 and then distilling from P_2O_5. THF was freshly distilled from Na/benzophenone, while CH_3CN either was purified as previously described[23] or was Aldrich HPLC grade (stored under N_2) and was used without further purification. The supporting electrolyte was tetra-*n*-butylammonium tetrafluoroborate—TBAF (prepared by the neutralization of aqueous TBA^+OH^- with HBF_4 and recrystallization of the product from $MeOH/H_2O$ by slow evaporation, followed by vaccum drying of the crystals). The electrolyte was generally used at between 0.05 and 0.2 M in all solutions. Solutions in the electrochemical cells were degassed with argon for 10–15 min prior to running a CV and were maintained under argon throughout the experiments.

Low-temperature CV's (down to −55 °C) were obtained by using a jacketed electrochemical cell and cooling with thermostatically controlled (Haake Q thermostat) methanol. For these experiments the Ag/AgCl(aq) reference electrode ceased to function below about −15 °C and was replaced with a silver wire pseudoreference, and ferrocene was added as an internal standard. The pseudoreference gave very reproducible results, and on this scale in THF the $E_{1/2}$ of ferrocene was +0.68 V and independent of temperature. The solution resistance of THF is exceptionally high, and on cooling this leads to substantial peak splittings for reversible electrochemical processes (e.g., Fc^+/Fc) even at very low currents.

Synthesis. Solvents were freshly distilled from a suitable drying agent (CaH_2 for CH_2Cl_2 and Na/benzophenone for THF). All other chemicals were reagent grade. Chemical oxidations were performed under N_2 by using standard Schlenk techniques. The preparation of $[N(PPh_3)_2]_2[Os_{10}C(CO)_{24}]$ (1) has been described previously.[24] Compounds 2–5 cannot be purified by TLC as they either slowly decompose or undergo air oxidation to regenerate the parent dianion (1).

Electrochemical Preparation of $[Os_{20}Hg_2(C)_2(CO)_{48}]^{2-}$ (2). $[N(PPh_3)_2]_2[Os_{10}C(CO)_{24}]$ (1) (20 mg, 0.0055 mmol) is added to 20 cm^3 of degassed CH_2Cl_2–0.2 M TBAF. Controlled potential electrolysis of this solution at a Hg pool at a potential of +0.78 V yields a new species (2) quantitatively as judged by IR. Crystals of this new osmium cluster were not obtained due to the presence of electrolyte. However, this product is believed to be $[Os_{20}(C)_2(CO)_{48}Hg_2]^{2-}$ on the basis of characterization by IR and FAB mass spectrum. IR (in CH_2Cl_2 at room temperature); ν(CO) 2092 w, 2064 s, 2015 s cm^{-1}. This should be compared to the spectrum of $[Os_{10}C(CO)_{24}HgCl]^-$: 2092 w, 2064 s, 2014 s cm^{-1} (same conditions). FAB mass spectrum: m/z 5608 corresponds to $[Os_{20}(C)_2(CO)_{48}Hg_2]$ using ^{192}Os.

Chemical Preparation of $[N(PPh_3)_2]_2[Os_{20}(C)_2(CO)_{48}Hg_2]$ (2). $[N(PPh_3)_2]_2[Os_{10}C(CO)_{24}]$ (20 mg, 0.0055 mmol) was dissolved in 20 cm^3 of CH_2Cl_2. An excess of Hg metal (ca. 10 g) and $AgBF_4$ (1.1 mg, 0.0056 mmol) were added, and the reaction was stirred for 2 h by which time IR spectroscopy showed the complete formation of 2. The solution was filtered through a porosity 4 sinter under N_2 to remove the excess mercury and then slowly

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[21] Reference 8, p 297.

[22] LeVanda, C.; Bechgaard, K.; Cowan, D. O.; Rausch, M. D. *J. Am. Chem. Soc.* **1977**, *98*, 2964.

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reduced in volume to about 5 cm^3. At −20 °C microcrystals of **2** (15 mg or 75% yield) were obtained after 2 days.

Characterization. The IR and FABS mass spectrum were identical with those of the electrochemically synthesized material. ^1H NMR (in CD_2Cl_2 at room temperature): δ 7.42–7.85 (m, 30 H). Microanal. Calcd for $C_{122}H_{60}O_{48}Hg_2Os_{20}N_2P_4$: C, 21.8; H, 0.90; N, 0.42. Found: C, 21.52; H, 0.93; N, 0.56. The PPh_3Me^+ and Ph_4As^+ salts of **2** were prepared in a similar yield.

Preparation of $[N(PPh_3)_2]_2[Os_{20}Hg(C)_2(CO)_{48}]$ (3). $[N(PPh_3)_2]_2[Os_{20}(C)_2(CO)_{48}Hg_2]$ (**2**) (20 mg, 0.0029 mmol) was dissolved in 10 cm^3 of CH_2Cl_2 and allowed to stand under N_2 for 1 week. The solution changed from brown to deep red, and crystals of **3** (17 mg, 89% yield) were deposited along with metallic mercury.

Characterization. IR (cm^{-1} in CH_2Cl_2): v(CO) 2072 m, 2057 s, 2005 s. FAB mass spectrum: m/z 5408 corresponds to $[Os_{20}(C)_2(CO)_{48}Hg]$ using ^{192}Os. Microanal. Calcd for $C_{122}H_{60}O_{48}HgOs_{20}N_2P_4$: C, 22.6; H, 0.93; N, 0.43. Found: C, 22.39; H, 1.04; N, 0.55. The PPh_3Me^+ and Ph_4As^+ salts of **3** were prepared in a similar yield.

Chemical Preparation of $[Os_{10}C(CO)_{24}]^{3-}$ (4). $[N(PPh_3)_2]_2[Os_{10}C(CO)_{24}]$ (**1**) (200 mg, 0.055 mmol) is dissolved in 60 cm^3 of thoroughly freeze–thaw–degassed THF. To this solution is added 1 cm^3 of a freshly prepared solution of sodium benzyl ketyl in THF (made from 13 mg of Na (0.55 mmol) and 105 mg of benzophenone (0.55 mmol) in 100 cm^3 of THF) over a period of 2–3 min (1 equiv of Na/benzophenone in THF) which results in a darkening of the solution. Careful monitoring of the IR of the reaction mixture (using spectroscopic cells flushed with argon) showed that the reaction was complete after about 5 min with near quantitative formation of **4**. On standing a mixture of **1** and **5** forms so crystals of **4** could not be obtained. The chemically prepared sample was characterized by IR spectroscopy (ν(CO) 2009 s, 1966 s cm^{-1} in CH_2Cl_2).

Electrochemical Preparation of $[Os_{10}C(CO)_{24}]^{4-}$ (5). $[N(PPh_3)_2]_2[Os_{10}C(CO)_{24}]$ (**1**) (20 mg, 0.0055 mmol) is added to 20 cm^3 of degassed CH_3CN–0.1 M TBAF. Controlled potential electrolysis of this solution at a Pt mesh at a potential of −1.40 V yields a new species (**5**) quantitatively as judged by IR. Crystals of this new osmium cluster could not be obtained due to the presence of electrolyte and the *extreme* oxygen sensitivity of **5**. However, repeating this preparation in CH_2Cl_2–0.1 M tetraethylammonium perchlorate caused deposition of microcrystals. This solid gave satisfactory microanalysis for $[TEA]_2[PPN]_2-[Os_{10}C(CO)_{24}]$, and on dissolving in THF-d_8 NMR signals consistent with the presence of both PPN^+ and TEA^+ were observed. This solid or its solution readily regenerated **1** in quantitative yield on standing in moist air for a matter of minutes. All this evidence supports the formulation of the reduced cluster as a tetraanion.

Characterization. IR (cm^{-1} in CH_3CN); ν(CO) 1989 s, 1941 s. FAB mass spectrum: m/z 2604 corresponds to $[Os_{10}C(CO)_{24}]$ using ^{192}Os. Microanal. Calcd for $C_{101}H_{80}O_{24}Os_{10}N_4P_4$ ($[NEt_4]_2[N(PPh_3)_2]_2[Os_{10}C(CO)_{24}]$): C, 32.09; H, 2.12; N, 1.48. Found: C, 32.31; H, 2.17; N, 1.53. ^1H NMR data recorded in THF-d_8 at room temperature: δ +1.62 (t), +3.04 (q), +7.36–7.64 (m).

Chemical Preparation of $[Os_{10}C(CO)_{24}]^{4-}$ (5). $[N(PPh_3)_2]_2[Os_{10}C(CO)_{24}]$ (**1**) (20 mg, 0.0055 mmol) is dissolved in 10 cm^3 of thoroughly freeze–thaw–degassed THF. To this solution is added, over a period of 30 min, 2 equiv of Na/benzophenone in THF. The solution changed from red-brown to black. Careful monitoring of the IR of this solution (using spectroscopic cells flushed with argon) showed that the reaction was complete after about 30 min with quantitative formation of **5**. Attempts to prepare crystals from this solution failed as in all cases **1** was regenerated. The chemically prepared sample was characterized by IR spectroscopy (ν(CO) 1988 s, 1940 s cm^{-1} in CH_2Cl_2). Attempts to obtain ^{13}C NMR data on this tetraanion (**5**) were frustrated by difficulties in the preparation of the ^{13}C-labeled $[Os_{10}C(CO)_{24}]^{2-}$.

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Registry No. 1, 75026-12-9; 1·$[N(PPh_3)_2]_2$, 75117-74-7; 2, 112548-69-3; 2·$[N(PPh_3)_2]_2$, 112595-82-1; 3, 106466-56-2; 4, 112352-96-2; 5, 112326-42-8; 5·$[NEt_4]_2[N(PPh_3)_2]_2$, 112533-53-6; $AgBF_4$, 14104-20-2; Hg, 7439-97-6; O_3, 7440-04-2; Pt, 7440-06-4; Au, 7440-57-5.

Organolithium Reagents in Metal Carbonyl Reduction Reactions. Syntheses of $HFe_3(\mu_2\text{-}COMe)(CO)_{10}$, $Fe_3(\mu_3\text{-}COMe)_2(CO)_9$, and $Fe_3(\mu_3\text{-}C{=}CH_2)(CO)_{10}$

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n-Butyllithium reduces the $Fe_3(CO)_{12}$ cluster, and on subsequent treatment with Me_3OBF_4 the compounds $HFe_3(\mu_2\text{-}COMe)(CO)_{10}$ (**2**), $Fe_3(\mu_3\text{-}COMe)_2(CO)_9$ (**3**), and $Fe_3(\mu_3\text{-}C{=}CH_2)(CO)_{10}$ (**1**) are formed. Similar reductions are possible with *t*-BuLi and PhLi. Compound **2** is thus obtained more simply and less dangerously than in a previously published procedure. Complex **3** is the first example where two μ_3-methylidyne methyl ether groups are symmetrically bound to a trinuclear cluster. Synthesis of **3** from **2** is also demonstrated. Similarly, compound **3** can be converted to **1**. The photochemical reactivity of **1** with H_2 and with (*E*)-cyclooctene is described. Compounds **1** and **3** have been characterized by an X-ray structure analysis. (**1**: $C_{12}H_2O_{10}Fe_3$, orthorhombic, space group $Pna2_1$, $a = 21.129$ (2) Å, $b = 9.079$ (1) Å, $c = 8.599$ (1) Å, $Z = 4$. **3**: $C_{13}H_6O_{11}Fe_3$, monoclinic, space group $P2_1/n$, $a = 8.606$ (1) Å, $b = 13.955$ (2) Å, $c = 14.899$ (1) Å, $\beta = 92.117$ (9)°, $Z = 4$.)

Introduction

Trinuclear cluster compounds of the nature $H_mM_3(CO)_nCX$ (M = Fe, Ru, Os, Co; X = H, Me, OMe, etc.; $m = 1–3$, $n = 9–11$) are rapidly gaining importance as model compounds for mechanistic studies on reactions of CO involving (1) C–C and C–H bond formations and (2) C–O

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