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Redox Properties of Trinuclear Osmium Carbonylhydride Clusters with Unsaturated Ligands

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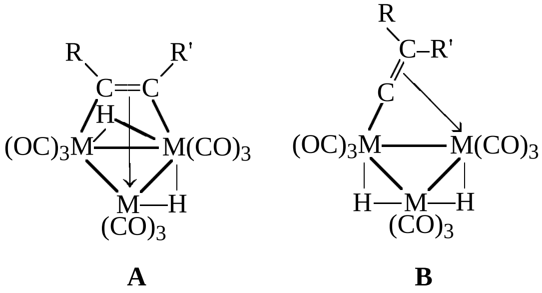
Abstract—Schemes of redox transformations were proposed for osmium carbonylhydride clusters: trinuclear $(\mu\text{-H})Os_3(\mu\text{-CR=CHR'})(CO)_{10}$ (R = R' = H, Ph; R = H, R' = Ph), $(\mu\text{-H})_2Os_3(\mu_3\text{-L})(CO)_9$ (L = C=CHPh, CH≡CPh), tetranuclear $CpMnOs_3$ $(\mu\text{-CH=CHPh})(\mu\text{-H})(\mu\text{-CO})(CO)_{11}$, and trinuclear $Os_3(\mu_3\text{-C=CHPh})(CO)_9$. Two-electron reduction of the trinuclear clusters results in elimination of the unsaturated ligand with preservation of the metal framework.

Owing to the presence of a group of metal atoms with a common electronic system, cluster compounds of transition metals are able to simultaneously coordinate and activate various substrates on closely located metal centers and to fairly easily donate and accept electrons. In this connection clusters are rather perspective candidates for polynuclear redox metal catalysis. Osmium clusters are known to catalyze isomerization of alkenes and dienes [1] and hydrogenation of CO [2]. To understand mechanisms of these reactions, it is necessary to study the inherent redox properties of the catalysts.

Electrochemical methods allow one to obtain quantitative information on special features of redox transformations of cluster compounds, to establish mechanisms of redox processes, and to correlate these data with the electronic structure of the compounds under study. We earlier studied the electrochemical behavior of certain mononuclear [3], bimetallic [4, 5], and cluster [5, 6] compounds containing Mn, Fe, Pd, Pt, and unsaturated organic ligands. Osmium carbonylhydride clusters with unsaturated ligands have never been explored by electrochemical methods.

The hydrogen atom in carbonylhydride clusters usually acts as a bridging ligand that connects two metal atoms in case of edge coordination or three metal atoms in case of face coordination.

Unsaturated organic ligands are essentially modified upon coordination on several metal centers [7–10]. Reactions of ruthenium and osmium trinuclear carbonyls with olefins give two types of clusters isomeric to each other. One of them (**A**) contains μ_3-acetylene as a bridging organic ligand and the other (**B**), μ_3-vinylidene.



M = Ru, Os.

Migration of hydrogen atoms between the ligand and M_3 framework plays a significant role in interconversions of olefin, acetylene, and vinylidene ligands on polynuclear centers. The metal framework of the cluster acts as a “hydrogen sponge,” participating in hydrogen transfer from one part of the molecule to another.

The aim of this work was to study electrochemically osmium clusters with unsaturated organic ligands, such as σ-, π-vinyl, σ-, σ-, π-vinylidene, and s-, σ-, π-acetylene. We fulfilled a comparative study of redox reactions of osmium trinuclear clusters containing no bridging hydrogen atoms: $Os_3(CO)_{12}$ (**I**), $Os_3(\mu_3\text{-C=CHPh})(CO)_9$ (**II**) and carbonylhydride clusters $(\mu\text{-H})Os_3(\mu\text{-CH=CHPh})(CO)_{10}$ (**III**), $(\mu\text{-H})Os_3(\mu\text{-CH=CH}_2)(CO)_{10}$ (**IV**), $(\mu\text{-H})Os_3\cdot(\mu\text{-CPh=CHPh})(CO)_{10}$ (**V**), $(\mu\text{-H})_2Os_3(\mu_3\text{-C=CHPh})\cdot(CO)_9$ (**VI**), $(\mu\text{-H})_2Os_3(\mu_3\text{-CH≡CPh})(CO)_9$ (**VII**), as well as a tetranuclear heterometallic cluster $CpMnOs_3\cdot(\mu\text{-CH=CHPh})(\mu\text{-H})(\mu\text{-CO})(CO)_{11}$ (**VIII**).

Electrochemical characteristics of clusters **I**–**VIII** are given in the table.

Electrochemical characteristics of osmium carbonylhydride clusters **II**–**VIII** with unsaturated ligands [Et_4NBF_4 in MeCN (*c* 0.1 M), Ag/$AgNO_3$ in MeCN (*c* 0.1 M)]

Comp. no.	Reduction, $E_{1/2}$, V (n)[a]			Oxidation, $E_{1/2}$, V (n)[a]
	1st wave	2nd wave	3rd wave	
I	–1.75[b] (1)	–2.77 (1)	–	0.90[b,c] (1)
II	–1.20 (1)	–1.35 (1)	–2.80(4)	0.67[c] (1)
III	–1.40 (2)	–2.33 (1)	–2.80 (~4)	–
IV	–1.52[b] (2)	–	–	–
V	–2.74 (6)	–	–	–
VI	–1.92 (2)	–2.56 (1)	–2.83 (~4)	0.23[c] (1)
VII	–2.12 (2)	–2.58 (1)	–2.84(4)	–0.33 (1)
VIII[d]	–1.72[b] (2)	–2.15 (1)	–2.52(1)	–0.15 (1)

[a] On a dropping mercury electrode, *n* is the number of electrons. [b] Reversible stage. [c] On a Pt electrode. [d] $E_{1/2}$ –2.80 V, *n* ~4 (4th wave).

Reduction and oxidation waves of clusters **I**–**VIII** are diffusion-controlled, as their limiting currents I_{lim} depend linearly on concentration (*c* 10^{-4}–10^{-3} M), mercury column height ($h^{-1/2}$ 25–65 cm), and potential scan rate ($V^{-1/2}$ 0.01–0.50 V s^{-1}).

As we showed earlier [11], cluster **I** with a regular triangle metal framework is reduced in acetonitrile on a dropping mercury electrode in two one-electron stages at –1.75 and –2.77 V. The first stage is reversible and gives rise to the radical anion $[Os_3(CO)_{12}]^{\dot{-}}$.

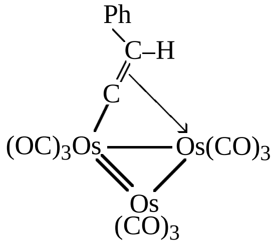
$$Os_3(CO)_{12} + \bar{e} \rightleftarrows [Os_3(CO)_{12}]^{\dot{-}}.$$

Further one-electron reduction of the radical anion proceeds irreversibly to give a dianion.

$$[Os_3(CO)_{12}]^{\dot{-}} + \bar{e} \longrightarrow [Os_3(CO)_{12}]^{2-}.$$

The ESR spectra of electrochemically generated 49-electron radical anions $[M_3(CO)_{12}]^{\dot{-}}$ (M = Fe, Ru, Os) [12] and quantum-chemical calculations of trinuclear clusters {$M_3(CO)_{12}$ [13] with the same metals} show that atomic orbitals (AO) of the metals contribute most to the lowest unoccupied molecular orbital (LUMO) of the clusters. Increase in the electronic density of the metal atoms upon substitution of electron-donor phosphorus-containing ligands (L = PPh_3, $P(OPh)_3$, $P(OMe)_3$) for carbonyl groups in $Fe_3(CO)_{12}$ increases the energy of LUMO that accepts electron on reduction and shifts the reduction potentials of $Fe_3(CO)_{12-n}L_n$ (*n* = 1–3) to the cathodic region [12].

The polarogram of cluster **II** contains three reduction waves at $E_{1/2}$ –1.20, –1.35, and –2.80 V.



II

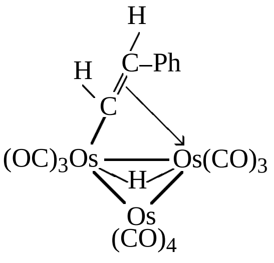
Switching polarography at *v* 50 Hz and cyclic voltammetry established that the reduction of cluster **II** is irreversible. The potential of the first one-electron reduction wave is shifted by 0.55 V to the anodic region as compared to cluster **I** (see table). Hence, the substitution of the π-acceptor phenylvinylidene ligand for carbonyl groups in compound **I** facilitates reduction of cluster **II** and renders it irreversible.

A special feature of the vinylidene complexes is they have two clearly pronounced differently charged centers: electrophilic (C^{α}) and nucleophilic (C^{β}) [8], i.e. the LUMO of these compounds in mainly concentrated on the C^{α} atom and HOMO, on the C^{β} atom of the vinylidene fragment. Hence, nucleophilic attack in reactions of these complexes is usually directed on C^{α} and electrophilic attack, on C^{β}. Probably, owing to the presence of an electrophilic center, cluster **II** is reduced easier than cluster **I** that lacks such a center.

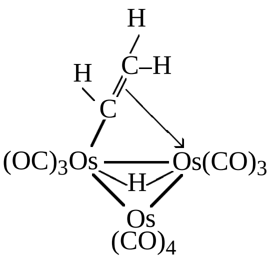
It is necessary to note that the second reduction wave of 46-electron cluster **II** has a maximum, and the height of the second cathodic peak in its cyclic voltammogram increases with increasing scan rate. Osella *et al.* [14] observed similar behavior in the electrochemical reduction of the trinuclear iron and osmium clusters with acetylene ligands $Fe_3(\mu_3\text{-CEt}{\equiv}\text{CEt})(CO)_9$ and $Os_3(\mu_3\text{-CPh}{\equiv}\text{CPh})(CO)_7[Ph_2P(CH_2)\cdot PPh_2]$. The osmium cluster is reduced in acetone in one quasi-reversible two-electron stage. The reduction of the $Fe_3(\mu_3\text{-CEt}{\equiv}\text{CEt})(CO)_9$ cluster proceeds in two consecutive completely reversible one-electron stages. The referees [14] explain such difference in the electrochemical behavior of these complexes by isomerization accompanying the first electron transfer in the iron cluster. It was found by NMR spectroscopy and cyclic fast-scanning voltammetry that one-electron reduction of the complex $Fe_3(\mu_3\text{-CEt}{\equiv}\text{CEt})(CO)_9$ is followed by isomerization of the radical anion $[Fe_3(\mu_3\text{-CEt}{\equiv}\text{CEt})(CO)_9]^{\dot{-}}$, involving reorientation of the ligand EtC≡CEt from perpendicular with respect to one of the Fe–Fe bonds of the triangular Fe_3 cycle to parallel. The second electron is then added to both isomers. This conclusion agrees with the theoretical calculations of Hoffmann and Wade [15, 16] who predicted that the alkyne should be perpendicular to one of the Fe–Fe bonds of the Fe_3 triangle in a 46-electron neutral cluster $Fe_3(\mu_3\text{-CEt}{\equiv}\text{CEt})(CO)_9$ be and parallel to it in a 48-electron dianion $[Fe_3 \cdot (\mu_3\text{-CEt}{\equiv}\text{CEt})(CO)_9]^{2-}$. Similar isomerizations have also been observed in other types of trinuclear complexes of transition metals [6, 14].

It is probable that the addition of one electron to cluster **II** results in isomerization of the radical anion $[Os_3(\mu_3\text{-C=CHPh})(CO)_9]^{\dot{-}}$ and reorientation of the ligand C=CHPh with respect to one of the Os–Os bonds of the Os_3 triangle. The second electron is then added to both isomers, which increases the limiting current of the second reduction wave.

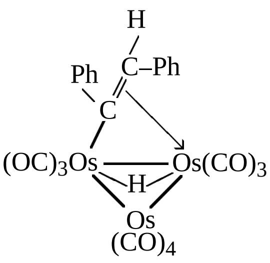
We have studied the electrochemical behavior of three osmium σ,π-vinyl carbonylhydride clusters **III**–**V**.



III



IV



V

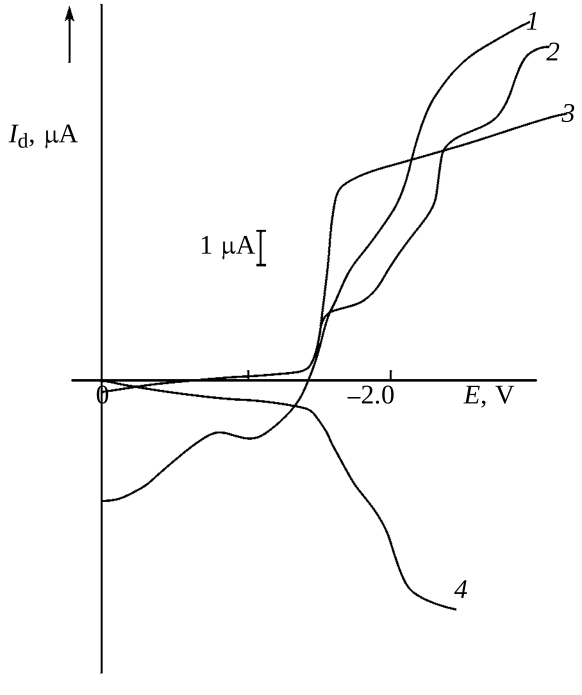
Unlike cluster **II**, cluster **III** which contains bridging hydride and phenylvinyl ligands is reduced in three successive irreversible stages at $E_{1/2}$ –1.40, –2.33, and –2.80 V with addition of two electrons in the first stage. The presence of a two-electron reduction wave points to a small difference in the potentials of the first and second electron transfers. At low scan rates (V < 0.5 V s^{-1}), the first two-electron wave at $E_{1/2}$ –1.40 splits into two one-electron waves at $E_{1/2}$ –1.36 and –1.46 V.

The potential of the first reduction wave of cluster **III** is shifted to the cathodic region by 0.20 V compared to cluster **II** (see table). It is probable that the hydrogen atom at the C^α atom of the phenylvinyl ligand decreases the positive charge on this carbon atom, rendering cluster **III** more difficult to reduce compared to cluster **II**.

Cluster **IV** is reduced in one reversible two-electron stage, as found by switching polarography at v 50 Hz (see figure, curves *1* and *4*) and cyclic voltammetry.

The reduction potential of cluster **IV** ($E_{1/2}$ –1.52 V) is shifted by 0.12 V to the cathodic region as compared to the $E_{1/2}$ of the first two-electron reduction wave of cluster **III** (see table). This may result from the presence of sterically less hindered than phenyl substituents at the C^α and C^β atoms of the vinyl ligand.

Cluster **V** is reduced in one partly reversible six-



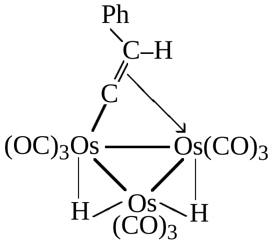
Polarogram of the cluster $(\mu\text{-H})Os_3(\mu\text{-CH=CH}_2)(CO)_{10}$ (**IV**) (0.1 M solution of Et_4NBF_4 in MeCN, 10^{-3} M, Ag/0.1 M solution of $AgNO_3$ in MeCN) (*1, 3, 4*) before and (*2*) after electrolysis at E_{aux} –1.70 V. For (*1*) and (*4*), see text. (*3*) Classical polarogram.

electron stage, the reduction being much more difficult ($E_{1/2}$ –2.74 V) compared to compounds **III** and **IV** (see table). It is probable that the presence of two bulky phenyl groups hampers electron attack of the C^{α} atom, as evidenced by the fact that the reduction potential $E_{1/2}$ is strongly shifted to the cathodic region.

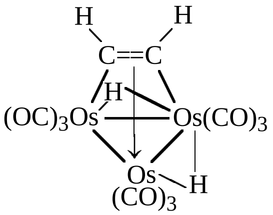
Koridze [9, 10] has shown that the regioselectivity of nucleophilic attack on various acetylide clusters is determined not only by the coordination mode of the acetylene ligand and by the electron density distribution on C^{α} and C^{β}, but also by steric factors.

Clusters **VI** and **VII** with two bridging hydride ligands and various unsaturated ligands (vinylidene and acetylene) are reduced by the same mechanism in three irreversible stages (see table).

The potential of the first two-electron reduction wave of cluster **VII** ($E_{1/2}$ –2.12 V) with the ligand CH≡CPh is slightly shifted to the cathodic region as compared to cluster **VI** containing the phenylvinylidene ligand C=CHPh ($E_{1/2}$ –1.92 V). Such behavior may be associated with a strong electron-acceptor power of phenylvinylidene, as well as with weaker steric hindrances phenylvinylidene creates in the ligand surrounding of the metal as compared to phenylacetylene.



VI



VII

Comparison of the potentials of the first reduction waves of clusters **III**, **IV**, **VI**, and **VII** containing bridging hydride ligands with the potential of hydride-free cluster **II** shows that the presence of hydride ligands is responsible for the more difficult reduction. Consequently, bridging hydride ligands in the clusters under study increase-energy of LUMO that accepts electron on their reduction.

To elucidate the mechanism of the electrochemical reduction of trinuclear clusters, we have carried out electrolysis of compounds **III**–**V** at controlled potential of the limiting current of the first two-electron reduction wave and identified the electrolysis products by polarography and IR spectroscopy.

It was found that after electrolysis of cluster **IV** (E_e –1.70 V) the reduction wave at $E_{1/2}$ –1.52 V disappears from the polarogram and a reduction wave at $E_{1/2}$ –2.33 appears (see figure, curve *2*). The one-electron reduction wave with the same potential, $E_{1/2}$ –2.33 V, is present in the polarogram of cluster **III** after its two-electron reduction (see table). In the polarogram of compound **V**, taken after electrolysis (E_e –2.80 V), a reduction wave at $E_{1/2}$ –2.33 V was also detected. Hence, two-electron reduction of clusters **III**–**V** yield the same product. This conclusion is confirmed by the IR spectra of working solutions taken after two-electron reduction of clusters **III**–**V**, which are identical in the region of ν_{CO} stretching vibrations.

It is characteristic that the reduction potential of the two-electron reduction product of clusters **III**–**V** coincides with the value $E_{1/2}$ –2.33 V corresponding to one-electron reduction of the complex $[(\mu\text{-H})Os_3 \cdot (\mu\text{-CO})(CO)_{10}]^-$ with no unsaturated organic ligands.

Except for the reduction wave at $E_{1/2}$ –2.33 V, the polarogram of cluster **V**, taken after electrolysis, contains reduction waves at $E_{1/2}$ –2.70 and –2.90 V, which is close to the $E_{1/2}$ of two-electron reduction waves of PhC≡CPh ($E_{1/2}$ –2.74 and –2.93 V) and PhHC=CHPh ($E_{1/2}$ –2.62 and –2.88 V). The polarogram of cluster **III** contains a four-electron reduction wave at $E_{1/2}$ of –2.80 V, which is close to the $E_{1/2}$ of two-electron reduction waves of HC≡CPh ($E_{1/2}$ –2.80 and –2.93 V) and CH_2=CHPh ($E_{1/2}$ –2.76 and –2.90 V).

The resulting data suggest that two-electron reduction of clusters **III** and **V** and electrolysis of cluster **IV** result in detachment of the unsaturated organic ligands and in formation of the dianion $[(\mu\text{-H})Os_3 \cdot (CO)_{10}]^{2-}$.

$$\underset{\textbf{III–V}}{(\mu\text{-H})Os_3(\mu\text{-CR=CHR}')(CO)_{10}} + 2\,\bar{e}$$

$$\longrightarrow [(\mu\text{-H})Os_3(\mu\text{-CR=CHR}')(CO)_{10}]^{2-}$$

$$\longrightarrow [(\mu\text{-H})Os_3(\mu\text{-CR=CHR}')(CO)_{10}]^{2-}$$

$$+\ 1/2\text{RC}\equiv\text{CR}'\ +\ 1/2\text{RHC=CHR}'.$$

The subsequent reduction stages involve addition of electrons to the dianion $[(\mu\text{-H})Os_3(CO)_{10}]^{2-}$ and to the molecules of acetylenes RC≡CR' and olefins RHC=CHR'.

Addition of six electrons to cluster **V** corresponds to a multistage process. The addition of two electrons in the first stage results in elimination of the unsaturated ligand which is reduced in the subsequent stages. The close potentials of the reduction waves of the cluster and the unsaturated ligand results in wave coalescence into one six-electron wave.

The equal numbers of electrons added to clusters **VI** and **VII** in potential-determining stages and the closeness of the potentials of the second and third reduction waves for cluster **VI** ($E_{1/2}$ –2.56 and –2.83 V) to the reduction potentials of cluster **VII** ($E_{1/2}$ –2.58 and –2.84 V) and of the $E_{1/2}$ values for the third waves of these clusters to the $E_{1/2}$ values of phenyacetylene reduction (see table) suggest that two-electron irreversible reduction of clusters **VI** and **VII** involves detachment of the unsaturated ligand to give the same $[(\mu\text{-H})_2Os_3(CO)_9]^{2-}$ dianion.

$$(\mu\text{-H})_2Os_3(\mu_3\text{-L})(CO)_9 + 2\bar{e}$$

$$\longrightarrow \underset{\textbf{VI, VII}}{[(\mu\text{-H})_2Os_3(\mu_3\text{-L})(CO)_9]^{2-}} \longrightarrow [(\mu\text{-H})_2Os_3(CO)_9]^{2-}$$

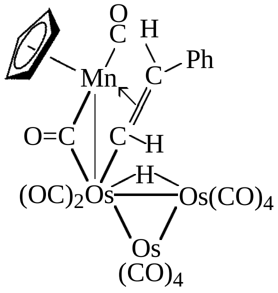
$$+ \ HC{\equiv}CPh.$$

The subsequent reduction stages are connected with electron additions to $[(\mu\text{-H})_2Os_3(CO)_9]^{2-}$ and HC≡CPh (see table).

After electrolysis of cluster **III** (E_e –1.60 V) the wave at $E_{1/2}$ –2.33 V disappears from the polarogram, the height of the wave at $E_{1/2}$ –1.40 V decreases, and a reduction wave at $E_{1/2}$ –2.56 V appears. Reduction waves with close $E_{1/2}$ potentials (–2.56 and –2.58 V) are present in the polarograms of clusters **VI** and **VII** (see table), implying that the complex $[(\mu\text{-H})Os_3\cdot(CO)_{10}]^{2-}$ formed by two-electron reduction of cluster **III** further converts to the complex $[(\mu\text{-H})_2Os_3(CO)_9]^{2-}$.

The electrochemical behavior of clusters **II**–**VII** agrees with their chemical behavior [17]. Reaction of cluster **IV** with CO yields $Os_3(CO)_{12}$. Reduction of cluster **IV** with hydrogen yields $(\mu\text{-H})_2Os_3(CO)_{10}$. Passing acetylene through a hexane solution of $(\mu\text{-H})_2Os_3(CO)_{10}$ at room temperature results in formation of $(\mu\text{-H})Os_3(\mu\text{-CH=CH}_2)(CO)_{10}$.

In this work we have studied tetranuclear heterometallic carbonylhydride cluster **VIII**. According to the X-ray diffraction data in [18], this compound belongs to a "triangle with a thorn" structural type, i.e. the manganese atom is attached to one of the osmium atoms of the trinuclear Os_3 cycle. The phenylvinyl ligand is σ-bound to an Os atom and π-coordinated to the Mn atom.



VIII

Cluster **VIII** is reduced in four successive stages at $E_{1/2}$ –1.72, –2.15, –2.52, and –2.80 V. The first two-electron wave is reversible, as found by switching polarography and cyclic voltammetry. Hence, the addition of two electrons to complex **VIII** results in formation of dianion **C**.

$$\underset{\textbf{VIII}}{CpMnOs_3(\mu\text{-CH=CHPh})(\mu\text{-H})(\mu\text{-CO})(CO)_{11}} + 2\bar{e}$$

$$\rightleftarrows \ \underset{\textbf{C}}{[CpMnOs_3(\mu\text{-CH=CHPh})(\mu\text{-H})(\mu\text{-CO})(CO)_{11}]^{2-}}.$$

The potentials of the second, third, and fourth reduction waves of cluster **VIII** are close to the $E_{1/2}$ of cluster **VII** (see table). Thus, we can assume that dianion **C** formed in the first stage decomposes into $[CpMn(CO)_2]^{2-}$ and cluster **III** which then converts to cluster **VII**.

$$\textbf{C} \longrightarrow [CpMn(CO)_2]^{2-} + \underset{\textbf{III}}{(\mu\text{-H})Os_3(\mu\text{-CH=CHPh})(CO)_{10}},$$

$$\textbf{III} \longrightarrow \underset{\textbf{VII}}{(\mu\text{-H})_2Os_3(\mu_3\text{-CH}{\equiv}\text{CPh})(CO)_9}.$$

The subsequent stages involve electron additions to cluster **VII**.

Our electrochemical data agree with the chemical behavior of cluster **VIII** [18, 19]. It readily loses the $[CpMn(CO)_2]^{2-}$ fragment in solutions to give a mixture of compounds **III** and **VII** at 20°C, whereas its thermolysis yields μ_3-vinylidene cluster **VI**.

We found that compounds **II** and **VI**–**VIII** can be both reduced and oxidized. The clusters are oxidized in one one-electron irreversible stage to form radical cations $[Q]^{\dot{+}}$.

$$Q - \bar{e} \ [Q]^{\dot{+}},$$

Q are clusters **II** and **VI–VIII**.

The oxidation potentials are displaced to the anodic region in the order **VII** < **VI** < **II** (see table). Similar regularity was also observed for the reduction potentials $E_{1/2}$ of the clusters under study, i.e. the more difficult a cluster is reduced, the easier it is oxidized.

Our comparative study of the redox properties of cluster compounds **II**–**VIII** with unsaturated organic ligands and the Os_3 triangular metal cycle as the main structural fragment allows the following conclusions.

Introduction of the π-acceptor phenylvinylidene ligands instead of carbonyl groups into trinuclear osmium clusters renders their reduction easier and irreversible. The presence of bridging hydride ligands in the trinuclear osmium clusters hampers their reduction. Two-electron reduction of the trinuclear clusters results in detachment of the unsaturated organic ligand with preservation of the cluster framework. Two-electron reduction of tetranuclear carbonylhydride compound **VIII** results in detachment of the $[CpMn(CO)_2]^{2-}$ fragment and formation of trinuclear osmium cluster **VII**.

It is necessary to note in conclusion that the easy formation of trinuclear carbonylhydride clusters with unsaturated ligands and the elimination of the unsaturated ligand during their reduction with preservation of the cluster framework suggest that such compounds can be effective catalysts and active intermediates in transformations of hydrocarbons on metal centers.

EXPERIMENTAL

Compounds **II**–**VIII** were obtained by the procedures in [18, 19].

Electrochemical measurements were carried out in argon at room temperature for freshly prepared solutions of compounds **I**–**XI** in acetonitrile purified as described in [20]. The background electrolyte was Et_4NBF_4 (c 0.1 M). The polarograms and cyclic voltammograms were recorded on an RA-3 polarographic analyzer using a three-electrode circuit. The potential scan rate was varied within 0.01–0.50 V s^{-1}. The working electrodes were a dropping mercury electrode with forced dropping (m 3.6 mg s^{-1}, τ 0.23 s) or a stationary platinum electrode 1 mm in diameter, embedded in Teflon (10 mm). For better reproducible properties, the platinum working electrode was polished with a felt-supported wet alumina of chromatographic grade before each measurement.

The reference electrode was $Ag/AgNO_3$ (c 0.1 M) in MeCN. It was connected to a cell by an electrolytic bridge filled with the background electrolyte. The auxiliary electrode was a platinum spiral embedded in a glass tube with a porous membrane.

The number of electrons participating in each reduction stage was determined by polarographic coulometry [21].

The switching polarograms were recorded using Kalousek's switch [22], switching frequency 50 Hz.

Controlled-potential electrolysis was carried out in an RA-3 polarographic analyzer using a three-electrode circuit. The working electrode was bottom mercury, surface area 4 cm^2. The reference electrode was $Ag/AgNO_3$ (c 0.1 M) in MeCN, and the auxiliary electrode was platinum. Electrolysis was carried out with vigorous stirring and argon barbotage.

ACKNOWLEDGMENTS

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