Redox behavior of trinuclear $M_3(\mu\text{-}H)(\mu_3\text{-}\eta^1{:}\eta^2{:}\eta^2\text{-}C_2Fc)(CO)_9$ and tetranuclear $RuM_3(\mu\text{-}H)(\mu_4\text{-}\eta^1{:}\eta^1{:}\eta^1{:}\eta^2\text{-}C_2Fc)(CO)_{12}$ (M = Ru or Os; and Fc = ferrocenyl) clusters. Electronic interaction between the ferrocenylacetylide ligand and the metal core of the cluster

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The redox properties of the clusters $Ru_3(CO)_{12}$ (**1**), $Ru_3(\mu\text{-}H)(\mu_3\text{-}\eta^1{:}\eta^2{:}\eta^2\text{-}C_2Fc)(CO)_9$ (**2**), $Os_3(\mu\text{-}H)(\mu_3\text{-}\eta^1{:}\eta^2{:}\eta^2\text{-}C_2Fc)(CO)_9$ (**3**), $Ru_4(\mu\text{-}H)(\mu_4\text{-}\eta^1{:}\eta^1{:}\eta^1{:}\eta^2\text{-}C_2Fc)(CO)_{12}$ (**4**), and $RuOs_3(\mu\text{-}H)(\mu_4\text{-}\eta^1{:}\eta^1{:}\eta^1{:}\eta^2\text{-}C_2Fc)(CO)_{12}$ (**5**) in THF have been studied by cyclic voltammetry in the temperature range from −60 to +20 °C. It was demonstrated that reversible one-electron oxidation of the ferrocenyl fragment in clusters **2**—**5** occurs at more positive potentials (ΔE^0 = 0.15—0.26 V) than that of free ferrocene. This is indicative of the electron-withdrawing character of the cluster core with respect to the ferrocenylacetylide ligand. The electron-withdrawing effect of the metal core is more pronounced in tetranuclear clusters **4** and **5** than in trinuclear clusters **2** and **3**. Unlike complexes **1**—**3**, which undergo irreversible reduction, complexes **4** and **5** undergo reversible one-electron reduction to form the corresponding radical anions $\mathbf{4}^{\cdot -}$ and $\mathbf{5}^{\cdot -}$.

Key words: ruthenium clusters, osmium clusters, osmium—ruthenium mixed clusters; ferrocenylacetylide ligand; cyclic voltammetry.

It is known that polydentate coordination of hydrocarbon moieties to several metal centers of transition-metal clusters has a pronounced effect on their reactivities.[1] Thus, under mild conditions, hydrocarbon ligands in acetylene and ethylene derivatives of the carbonyl clusters of metals add not only N- and P-nucleophiles[2,3] but uncharged C-nucleophiles as well.[4,5] It is evident that studies of the mutual electronic effect of the hydrocarbon ligands and the metal core in the clusters is of interest for an understanding of both the increased reactivities of these ligands and conversions of hydrocarbon substrates on the surface of heterogeneous catalysts. It is also known that because ferrocene can oxidize reversibly, the ferrocene-ferricenium system is a very sensitive indicator for studying the electronic properties of the substituents in the cyclopentadienyl ring as well as for estimating the degree of electronic interactions of different redox centers, which are present in a single molecule.[6,7] Therefore, studies of the redox properties of ferrocene-containing clusters is of obvious interest. In principle, the electronic interaction between two centers of one molecule should be accompanied by a change in the redox properties of these centers.[7] These data are most convenient to obtain by cyclic voltammetry.

Therefore, in this work we studied the redox behavior of ruthenium carbonyl $Ru_3(CO)_{12}$ (**1**), its ferrocenylacetylide derivative, namely, the trinuclear $Ru_3(\mu\text{-}H)(\mu_3\text{-}\eta^1{:}\eta^2{:}\eta^2\text{-}C_2Fc)(CO)_9$ cluster (**2**),[8,9] the triosmium analog $Os_3(\mu\text{-}H)(\mu_3\text{-}\eta^1{:}\eta^2{:}\eta^2\text{-}C_2Fc)(CO)_9$ (**3**),[9,10] and the tetranuclear clusters with a "butterfly" core, $Ru_4(\mu\text{-}H)(\mu_4\text{-}\eta^1{:}\eta^1{:}\eta^1{:}\eta^2\text{-}C_2Fc)(CO)_{12}$ (**4**)[11,12] and $RuOs_3(\mu\text{-}H)(\mu_4\text{-}\eta^1{:}\eta^1{:}\eta^1{:}\eta^2\text{-}C_2Fc)(CO)_{12}$ (**5**).[11,12] These compounds contain two redox-active centers, namely, the metal core and the ferrocene unit, and are convenient models for studying the redistribution of the electron density upon coordination of acetylide ligands on the surface of the metal cluster.

The ^1H and ^{13}C NMR spectra of clusters **4** and **5** are temperature-dependent due to fluctuations of the new type of acetylide ligand.[11,12] These spectral data are also indicative of a substantial deshielding of the nuclei of the ferrocenyl group compared to those of clusters **2** and

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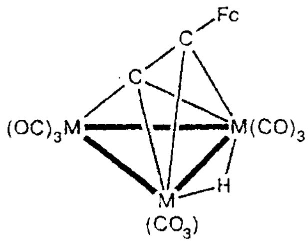
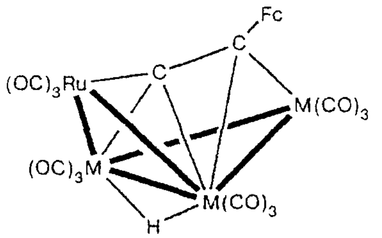


2, 3

M = Ru (**2**), Os (**3**)



4, 5

M = Ru (**4**), Os (**5**)

3, which may indicate that the transfer of the electron density from the acetylide ligand to the metal core is more efficient in the tetranuclear clusters than in the trinuclear clusters. Therefore, it is of interest to estimate the electronic interaction between the ferrocenylacetylide group and the metal core in these clusters by an independent method.

Experimental

The $Ru_3(\mu\text{-}H)(\mu_3\text{-}\eta^1:\eta^2:\eta^2\text{-}C_2Fc)(CO)_9$ (**2**), $Os_3(\mu\text{-}H)(\mu_3\text{-}\eta^1:\eta^2:\eta^2\text{-}C_2Fc)(CO)_9$ (**3**), $Ru_4(\mu\text{-}H)(\mu_4\text{-}\eta^1:\eta^1:\eta^1:\eta^2\text{-}C_2Fc)(CO)_{12}$ (**4**), and $RuOs_3(\mu\text{-}H)(\mu_4\text{-}\eta^1:\eta^1:\eta^1\eta^2\text{-}C_2Fc)(CO)_{12}$ (**5**) clusters were synthesized according to known procedures.[8—12]

Voltammetric measurements were carried out under a dry inert atmosphere in THF (Aldrich) that had been prepurified and distilled directly into an electrochemical cell (evacuated and filled with argon) according to the procedure described previously.[13] A solution of Bu_4NPF_6 (0.1 *M*) was used as the supporting electrolyte. Tetrabutylammonium hexafluorophosphate (Aldrich) was preliminarily dehydrated by melting *in vacuo*. Low-temperature electrochemical measurements were performed using a cell thermostatically controlled with isopropyl alcohol, which was cooled with liquid nitrogen in a Dewar vessel.

All measured potentials are given relative to an aqueous saturated calomel electrode by comparing the potential of the reference electrode (Ag/AgCl/4 *M* aqueous solution of LiCl), which was separated from the solution studied by a bridge filled with a solution of the supporting electrolyte, with the potential of the redox transformation of decamethylferrocene$^{0/+}$ (E^0 = 0.00 V, saturated calomel electrode).

A 1-mm disk platinum electrode or a 10—20-μm ultramicroelectrode sealed into glass and polished off with diamond paste (the grain size was ≤1 μm) were used as working electrodes. Voltammetric measurements were carried out using a PAR 175 generator of signals and a PAR 173 potentiostat with compensation of ohmic losses. Voltammograms were recorded on a two-coordinate RE0074 recorder.

Results and Discussion

Two anodic (*A*/*A*′ and *B*/*B*′) and six cathodic (*C*/*C*′, *D*, *E*, *F*, *G*, and *H*) peaks, which have different heights and different degrees of reversibility, are observed in the cyclic voltammograms of cluster **4** (Fig. 1, curve *3*). This cluster is unstable even in the crystalline state and contains its precursor **2** and ruthenium carbonyl **1** as impurities. Therefore, the electrochemical behavior of clusters **1** and **2** was preliminarily studied with the aim of identifying peaks *A*—*H*. It should be noted that all peaks observed in the voltammograms of complexes **1**—**5** under study are diffusion-controlled because $I_p \cdot v^{-1/2}$ = const (I_p is the peak height, and v is the rate of the linear potential scan).

Irreversible cathodic peaks *D* and *H* with approximately equal heights (see Fig. 1, curve *1*) are observed in the cyclic voltammogram of cluster **1**. The irreversible character of these peaks is retained even when the temperature decreases to −50 °C, which indicates that products of reduction of **1** are unstable. According to the data reported in Ref. 14, reduction of cluster **1** is described by the *EC* scheme (*E* and *C* are the electrochemical and chemical stages, respectively). According to this scheme, one-electron reduction of **1** is accompanied by a series of chemical transformations of radical anion $\mathbf{1}^{\cdot-}$ to form electroactive particles as a consequence of which the height of peak *D* is intermediate between the heights of the one- and two-electron peaks. In this work, we did not seek to elucidate the mechanism of reduction of cluster **1** in detail. We assigned peaks *D* and *H* in the cyclic voltammogram of cluster **4**

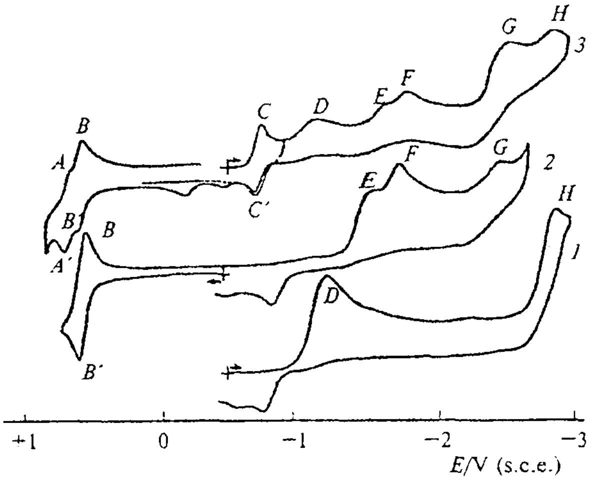


Fig. 1. Cyclic voltammograms of complexes **1** ($1.4 \cdot 10^{-3}$ mol L^{-1}; +5 °C; curve *1*), **2** ($1.2 \cdot 10^{-3}$ mol L^{-1}; +10 °C; curve *2*), and **4** ($7.7 \cdot 10^{-4}$ mol L^{-1}; −25 °C; curve *3*) in THF (0.1 mol L^{-1} Bu_4NPF_6) on a Pt electrode (v = 0.2 V s^{-1}).

Table 1. Oxidation and reduction potentials of clusters **1**—**5** and ferrocene in THF/0.1 mol L^{-1} Bu_4NPF_6 on a Pt electrode (υ = 0.2 V s^{-1}) at different temperatures[a]

Compound	T/°C	E^0 $(E_p)^b$/V (s.c.e.)							
		A/A'	*B/B'*	*C/C'*	*D*	*E*	*F*	*G*	*H*
$Ru_3(CO)_{12}$ (**1**)	+5				(−1.24)				(−2.88)
	−54				(−1.39)				(−2.94)
$Ru_3H(C_2Fc)(CO)_9$ (**2**)	−5		+0.59			(−1.64)	(−1.82)	(−2.57)	
	−50		+0.59			(−1.81)[c]			
$Os_3H(C_2Fc)(CO)_9$ (**3**)	−27		+0.64						
$Ru_4H(C_2Fc)(CO)_{12}$ (**4**)	−25	+0.70	+0.59	−0.76	(−1.20)	(−1.63)	(−1.80)	(−2.57)	(−2.88)
						(−2.08)[c]			
$RuOs_3H(C_2Fc)(CO)_{12}$ (**5**)	−18	+0.70		−0.91					
$Fe(C_5H_5)_2$	+5	+0.44							

[a] Slight differences in the potentials of the irreversible peaks in the table and in Figs. 1 and 2 are due to the different temperatures at which the voltammograms were recorded.

[b] The potentials of the irreversible peaks are given in parentheses.

[c] The potentials of peaks *E*+*F*.

to reduction of cluster **1**, which is present in compound **4** as an impurity (see below).

The voltammograms of cluster **2** (see Fig. 1, curve *2*) are characterized by the presence of irreversible cathodic peaks *E*, *F*, and *G* and the reversible anodic redox pair *B/B'* ($\Delta E_p = E_p{}^a - E_p{}^c$ = 55 mV at +10 °C, where $E_p{}^a$ and $E_p{}^c$ are the potentials of the anode and cathode responses, respectively). It is safe to suggest that the pair of peaks *B/B'* is associated with reversible one-electron oxidation of the ferrocene unit of cluster **2** because the redox potentials of this pair and of the free ferrocene have close values (Table 1). This makes it possible to use the height of one-electron anodic peak *B* as the internal standard for estimating the number of transferred electrons at potentials of cathodic peaks. Peak *E* is comparable in height to peak *B*, *i.e.*, it is a one-electron peak. Although the ratio of the heights of peaks *F* and *B* is 1.5—1.6, this fact may be determined by substantial overlapping of peaks *E* and *F*, and peak *F* can confidently be considered also as a one-electron peak. Note that peaks *E* and *F* remain irreversible even when the temperature decreases to −50 °C (under these conditions, peaks *E* and *F* merge into one irreversible two-electron peak), which indicates that products of one- and two-electron reduction of cluster **2** are unstable. It is most likely that reduction of **2** at the potentials of peaks *E* and *F* is described by the *ECE* or *ECEC* schemes, while the nature of the short peak *G* observed in the cyclic voltammogram of cluster **2** (see Fig. 1, curve *2*) is presently hard to interpret. It can be suggested that this peak is associated with reduction of the products that formed at the potentials of peaks *E* and *F*. At $T \le -50$ °C, this peak virtually disappears in the voltammograms.

The above-discussed data allow us to assign reliably peaks *A/A'* and *C/C'* in the voltammograms of cluster **4** (see Fig. 1, curve *3*) to redox processes with the participation of this cluster. Quite apparently, the pair of peaks *A/A'* corresponds to reversible (ΔE_p = 70 mV at −25 °C) one-electron oxidation of the ferrocene unit of cluster **4**, whereas peaks *C/C'* are associated with reversible (ΔE_p = −60 mV at −25 °C) one-electron reduction of the cluster core of the molecule. Although the presence of an impurity of **2** in a solution of **4** resulting in the pair of peaks *B/B'* in the cyclic voltammogram does not allow one to use the height of peak *A* as the internal standard for determining the electronic character of peak *C*, this peak (as will be demonstrated below by the example of isostructural cluster **5**) is a one-electron peak. Radical anion $\mathbf{4}^{\cdot -}$ generated at the potentials of peak *C* is stable within the cyclic voltammetry time scale even at room temperature, which is evidenced by the identical values of the heights of the cathode (*C*) and anode (*C'*) responses. The presence of impurities of **1** and **2** in a solution of **4**, which are responsible for peaks *D* and *H*, respectively (as well as for peaks *E*, *F*, and *G*), hinder identification of other cathodic peaks, which probably occur in the cyclic voltammogram of cluster **4** and which are associated with its further reduction. Nevertheless, the data obtained allow one to interpret qualitatively the mutual effect of the ferrocenylacetylide ligand and the cluster core on the redox properties of these two redox centers (see below).

Clusters **3** and **5**, which contain the $Os_3(CO)_9$ fragment and are isostructural to complexes **2** and **4**, respectively, were also studied for comparison. The quasi-reversible pair of peaks *B/B'*, which corresponds to oxidation of the ferrocene unit, and irreversible cathodic peak *E*+*F* are observed in the cyclic voltammogram of cluster **3** (Fig. 2, curve *1*). The height of the irreversible peak *E*+*F* at room temperature is 1.5—1.6 times larger than that of the one-electron peak *B*, which is indicative of its two-electron character. It can be suggested that

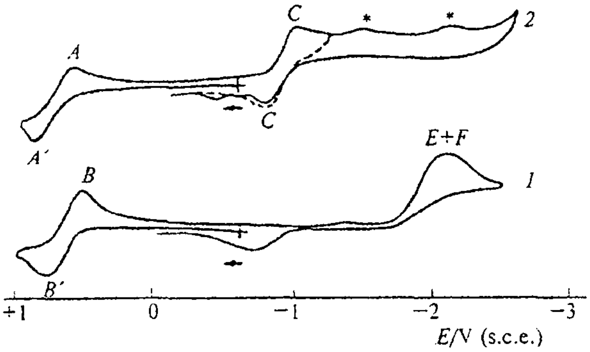


Fig. 2. Cyclic voltammograms of complexes **3** ($2.1 \cdot 10^{-3}$ mol L^{-1}; −27 °C; curve *1*) and **5** ($9 \cdot 10^{-4}$ mol L^{-1}; −18 °C; curve *2*) in THF (0.1 mol L^{-1} Bu_4NPF_6) on a Pt electrode (v = 0.2 V s^{-1}). The peaks at −1.52 and −2.18 V, which are probably associated with further reduction of cluster **5**, are marked with asterisks.

the electrode process at the potentials of this peak is described by the *ECE* or *ECEC* scheme identical to that of the reduction of ruthenium analog **2** at the potentials of overlapping one-electron peaks *E* and *F* (see above).

Redox processes of cluster **5** (see Fig. 2, curve *2*) involve reversible or quasi-reversible one-electron oxidation of the ferrocene unit (peaks *A*/*A*′) and reduction of the cluster core of the molecule (peaks *C*/*C*′). The one-electron character of reduction of complex **5** to radical anion $5^{\cdot -}$ is confirmed by the identical values of the heights of peaks *A* and *C*. Note that, unlike the tetraruthenium analog, radical anion $5^{\cdot -}$ is kinetically less stable because the values of the cathode (*C*) and anode (*C*′) responses become equal only at $T < 0$ °C. However, in the case of cluster **4**, the corresponding radical anion is stable within the cyclic voltammetry time scale even at room temperature (see above). Presently, it is difficult to interpret the nature of the small cathodic peaks at potentials of −1.52 and −2.18 V (marked with asterisks in Fig. 2, curve *2*). Apparently, these peaks are associated with further reduction of cluster **5**.

The values of the formal standard potentials $E^0 = (E_p{}^c + E_p{}^a)/2$ for redox pairs *A*/*A*′, *B*/*B*′, and *C*/*C*′ and potentials $E_p{}^c$ of irreversible peaks *D*—*H* for complexes **1**—**5** are given in Table 1. For free ferrocene, the value of E^0 in THF is 0.44 V. (For ferrocenylacetylide, the corresponding half-wave potential is 0.12 V.[15]) Therefore, the more positive values of E^0 for redox pairs *A*/*A*′ and *B*/*B*′ of clusters **2**—**5** prove unambiguously the electron-withdrawing character of the cluster core with respect to the ferrocene unit and, hence, the rather strong electronic interaction between these two redox centers. In going from ruthenium complex **2** to osmium analog **3**, the electron-withdrawing properties of the trinuclear $M_3(CO)_9$ core are enhanced, which manifests itself in the shift of the value of $E^0(B/B')$ for cluster **3** to more positive potentials by 0.05 V. In turn, replacement of the $Ru_3(CO)_9$ fragment by the $Os_3(CO)_9$ fragment in tetranuclear complex **4** is not accompanied by an increase in the electron-withdrawing properties of the cluster core, which is evidenced by the equal values of $E^0(A/A')$ for clusters **4** and **5** (see Table 1). Because $E^0(A/A') > E^0(B/B')$, the tetranuclear $M_4(CO)_{12}$ fragment exhibits stronger electron-withdrawing properties than the trinuclear $M_3(CO)_9$ complex. Finally, the anodic character of waves *A* and *B* recorded on 10—20-μm platinum ultramicroelectrodes indicates that, despite the strong electronic interaction between the redox centers, the complete transfer of an electron from the ferrocene unit to the cluster core does not occur. Therefore, as in the case of the $Ru_6C(CO)_{15}\{\mu\text{-}Fe(C_5H_4PPh_2)_2\}$ cluster,[16] the orbitals of the ferrocene unit make the major contribution to the highest occupied molecular orbitals (HOMO) of clusters **2**—**5**, although the more negative values of E^0 for free ferrocene (ΔE^0 = 0.15—0.26 V) indicate that the orbitals of the cluster core also make a substantial contribution to HOMOs.

The important characteristic feature of tetranuclear clusters **4** and **5** is their ability to undergo one-electron reduction to the corresponding radical anions stable within the cyclic voltammetry time scale. In going from tetraruthenium cluster **4** to heterometal analog **5**, the value of $E^0(C/C')$ shifts to more negative potentials (see Table 1). This is indicative of the lower energy of the lowest unoccupied molecular orbital (LUMO) of cluster **4**. It can be suggested that the LUMOs of ferrocene-containing clusters studied in this work as well as the LUMO of the $Ru_6C(CO)_{15}\{\mu\text{-}Fe[C_5H_4PPh_2]_2\}$ compound[16] have principally the character of the orbitals of the cluster core although they, apparently, contain an admixture of orbitals of the ferrocene unit.

In conclusion, note that the primary aim of this work was to determine the degree of the electronic interaction of two redox centers, which are present in clusters **2**—**5**. Therefore, we did not study the mechanism of reduction of the clusters at the potentials of peaks *D*—*H* in detail, and we did not consider the nature of the resulting products whose oxidation is observed in the anodic branches of the cyclic voltammograms (see Figs. 1 and 2). These questions are of separate interest and call for special studies. On the whole, the data obtained are indicative of the transfer of the electron density from the ferrocenylacetylide ligand to the metal core as well as of the fact that this transfer is more efficient in tetranuclear clusters **4** and **5** than in trinuclear clusters **2** and **3**. The last-mentioned fact is consistent with the data of the ^1H spectra of clusters **2**—**5**.[8—12] Therefore, the "carbocationic" character of the acetylene C atoms in reactions with nucleophiles would be expected to be more pronounced in tetranuclear clusters related to compounds **4** and **5**.

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