Reactivity of 17- and 19-electron organometallic complexes. Formation of bent sandwich 19-electron radical cation complexes of ruthenium and osmium

S. V. Kukharenko,[a] V. V. Strelets,[a] L. I. Denisovich,[b] M. G. Peterleitner,[b]**
A. Z. Kreindlin,[b] A. R. Kudinov,[b] and M. I. Rybinskaya[b]

[a]*Institute of Chemical Physics in Chernogolovka, Russian Academy of Sciences,*
142432 Chernogolovka, Moscow Region, Russian Federation.
Fax: +7 (096) 515 3588
[b]*A. N. Nesmeyanov Institute of Organoelement Compounds, Russian Academy of Sciences,*
28 ul. Vavilova, 117813 Moscow, Russian Federation.
Fax: +7 (095) 135 5085

The redox behavior of sandwich indenyl complexes of the general formula $(\eta^5\text{-}C_9H_7)ML$ (M = Ru and L = $\eta^5\text{-}C_9H_7$ (**1**), $\eta^5\text{-}C_5H_5$ (**2**), $\eta^5\text{-}C_5Me_5$ (**3**); M = Os, L = $\eta^5\text{-}C_9H_7$ (**4**)) has been studied in THF, MeCN, and CH_2Cl_2 by cyclic voltammetry and controlled potential electrolysis on a Pt electrode in the −85 to +20 °C temperature range. The title complexes have been found to undergo reversible one-electron oxidation to the corresponding radical cations, whose stabilities and reactivities depend on the nature of both the metal and π-ligands and of the nucleophilic properties of the solvent. The fast interaction of the electrogenerated 17-electron radical cations with nucleophiles yields bent sandwich 19-electron radical cations, $[(\eta^5\text{-}C_9H_7)M(L)(Nu)]^{+\cdot}$ (Nu = Cl^-, MeCN, or THF), the latter undergoing one-electron oxidation to the corresponding $[(\eta^5\text{-}C_9H_7)M(L)(Nu)]^{2+}$ dications. In the case of Nu = THF, the reaction of the electrogenerated 17-electron radical cations with nucleophiles appears to be reversible. Radical cations $[(\eta^5\text{-}C_9H_7)_2M]^{+\cdot}$ (M = Ru, Os) have been characterized by ESR spectra.

Key words: ruthenium and osmium complexes, cyclic voltammetry, electrochemical reactions.

The electrochemical oxidation of bis-cyclopentadienyl compounds and their decamethyl-substituted homologs is most studied for the series of sandwich complexes of iron group metals with η^5-coordinated ligands.[1,2] The reactivity of 17-electron radical cations formed as primary products upon this oxidation depends on the nature of both the metal atoms and π-ligands and determines the mechanism of electrooxidation of these complexes. The study of redox reactions of sandwich complexes of iron group metals with other η^5-coordinated ligands, in particular, polycyclic ligands, was only casual. For example, the potentials of the electrochemical oxidation of iron[3—5] and ruthenium[6] η^5-indenyl and η^5-fluorenyl complexes are known. Some reactions of 17-electron radical cations have been studied, with dibenzoferrocene as an example.[4,5] However, the data available do not allow one to perform comparative analysis of the main regularities of redox reactions of sandwich complexes of iron group metals with η^5-coordinated polycyclic ligands. To solve this problem using η^5-indenyl complexes as an example we have studied the electrochemical behavior of complexes of the general formula $(\eta^5\text{-}C_9H_7)ML$, where M = Ru, L = $\eta^5\text{-}C_9H_7$ (**1**), $\eta^5\text{-}C_5H_5$ (**2**), $\eta^5\text{-}C_5Me_5$ (**3**); M = Os, L = $\eta^5\text{-}C_9H_7$ (**4**), by cyclic voltammetry and preparative controlled potential electrolysis in media of aprotic solvents with various coordination abilities (THF, CH_2Cl_2, and MeCN).

Results and Discussion

Two diffusionally controlled anodic one-electron peaks are observed on cyclic voltammograms of ruthenium and osmium indenyl complexes **1—4** obtained on a Pt electrode in CH_2Cl_2 in the temperature range from −80 to 20 °C (Fig. 1, *a*, Table 1). The first peak has the corresponding cathodic response ($\Delta E_p = E_p^a - E_p^c$ = 60 mV, $I_p^a/I_p^c = 1$, 20 °C; E_p^a, I_p^a, E_p^c, I_p^c are the potentials and the heights of the anodic and cathodic peaks), which testifies to the chemical and electrochemical reversibility of the oxidation of the initial complexes to the corresponding 17-electron radical cations.* The

---

* The degree of chemical reversibility of oxidation (*i.e.*, the stability of radical cations formed) depends on the nature of the ligand and metal and on the experimental conditions. For example, reversible oxidation of **1**, **2**, and **4** is observed at room temperature, while complex **3** is oxidized reversibly only at $T < -20$ °C.

Translated from *Izvestiya Akademii Nauk. Seriya Khimicheskaya,* No. 12, pp. 2394—2399, December, 1995.

preparative oxidation of the above methioned complexes, studied using complex **1** as an example, is accompanied by the consumption of 1 F mol^{-1} of electricity and results in the formation of a dark-green solution of a paramagnetic complex, which is stable in an argon atmosphere for several hours and is characterized by its ESR spectrum ($g_\perp$ = 2.622, $g_\parallel$ = 1.990). The reduction of the oxidized solution results in the regeneration of complex **1** in a high yield (85—90 %). The oxidation of 17-electron radical cations at the potentials of the second anodic peak is irreversible at temperatures down to −80 °C, which follows from the absence of the corresponding cathodic responses in the temperature range studied. This indicates that 16-electron dications are extremely unstable even in such a weakly coordinating solvent as CH_2Cl_2. Thus, the oxidation of complexes **1—4** in CH_2Cl_2 can be presented by Scheme 1.

Scheme 1

$$(\eta^5\text{-}C_9H_7)ML \overset{-e}{\rightleftharpoons} [(\eta^5\text{-}C_9H_7)ML]^{+\cdot} \xrightarrow{-e} [(\eta^5\text{-}C_9H_7)ML]^{2+}$$

(18 *e*) (17 *e*) (16 *e*)

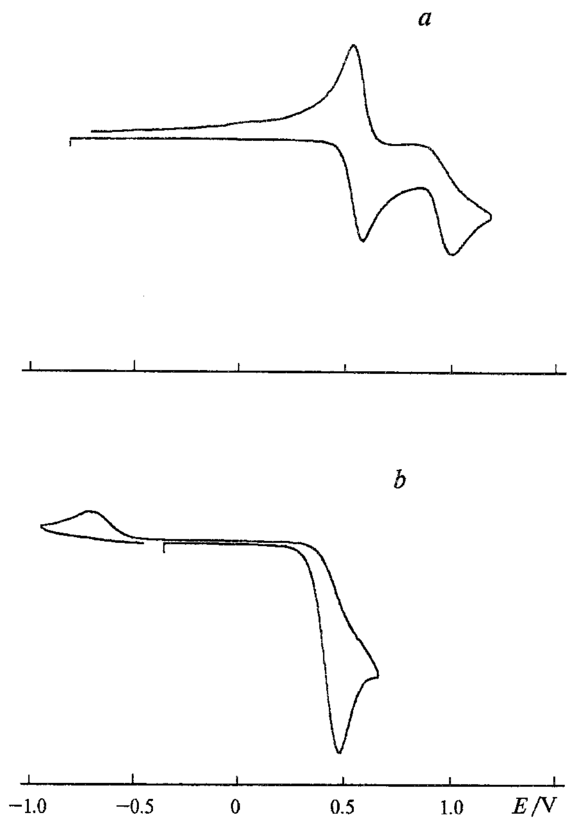


Fig. 1. Cyclic voltammograms of complex **1** (Pt electrode, V = 200 mV s^{-1}, T = 20 °C) in CH_2Cl_2/0.1 mol L^{-1} of Bu_4NPF_6 (*a*) and CH_2Cl_2/0.1 mol L^{-1} of Bu_4NPF_6 in the presence of a fivefold excess of $Cl^-(Et_3PhCH_2NCl)$ (*b*).

The mechanism of electrooxidation of complexes **1—4** changes substantially on going from CH_2Cl_2 that almost does not manifest nucleophilic properties (DN ≈ 0 7)) to comparatively strongly coordinating solvents. For example, in MeCN all complexes studied undergo the one-step two-electron irreversible oxidation rather than one-electron oxidation (Fig. 2, see Table 1). The cathodic peaks corresponding to the reduction of the products of the two-electron oxidation of complexes **1—4** appear on the reverse branch of the potential scan of the cyclic voltammograms of the compounds studied in MeCN. This unambiguously indicates that the solvent takes part in the electrodic reaction. Similar effect caused by the participation of a solvent has been observed previously for the oxidation of $(\eta^6\text{-}C_6H_3Me_3)W(CO)_3$.[8]

Table 1. Oxidation potentials E^0 (V, relative to SCE) of ruthenium and osmium sandwich L_1ML_2 complexes with η^5-indenyl and η^5-cyclopentadienyl ligands in various solvents

Complex	L_1	M	L_2	Solvent			
				CH_2Cl_2		THF,	MeCN,
				0/+	+/2+[a]	0/2+[b]	0/2+[c]
1	C_9H_7	Ru	C_9H_7	0.55	1.00	0.61	0.58
2	C_9H_7	Ru	C_5H_5	0.77	1.11	0.69	0.77
3	C_9H_7	Ru	C_5Me_5	0.53	0.95	0.60	0.55
4	C_9H_7	Os	C_9H_7	0.43	1.13	0.47[d]	0.47
	C_5H_5	Ru	C_5H_5	0.99[13]	—	0.93[c,14]	—
	C_5Me_5	Ru	C_5Me_5	0.53[2]	1.15	0.63[d]	—

[a] Irreversible one-electron oxidation, potential of the peak. [b] Reversible two-electron oxidation. [c] Irreversible two-electron oxidation, potential of the peak. [d] Reversible one-electron oxidation.

The electrochemical behavior of complexes **1—4** was studied in THF to elucidate the mechanism of the reaction of nucleophiles in the process of electrooxidation of these complexes. Although THF is more nucleophilic (DN = 20.0 7)) than MeCN (DN = 14.4 7)), the latter, as known, reacts readily with electrophiles. The high

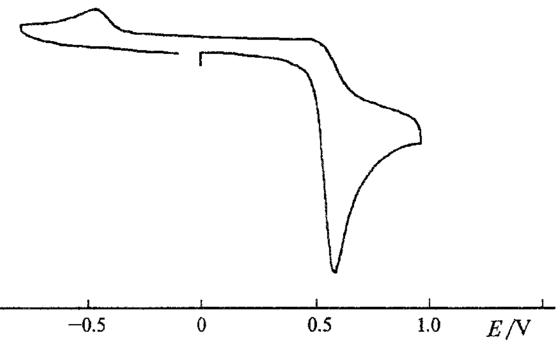


Fig. 2. Cyclic voltammogram of complex **1** (MeCN/0.1 mol L^{-1} of Bu_4NPF_6).

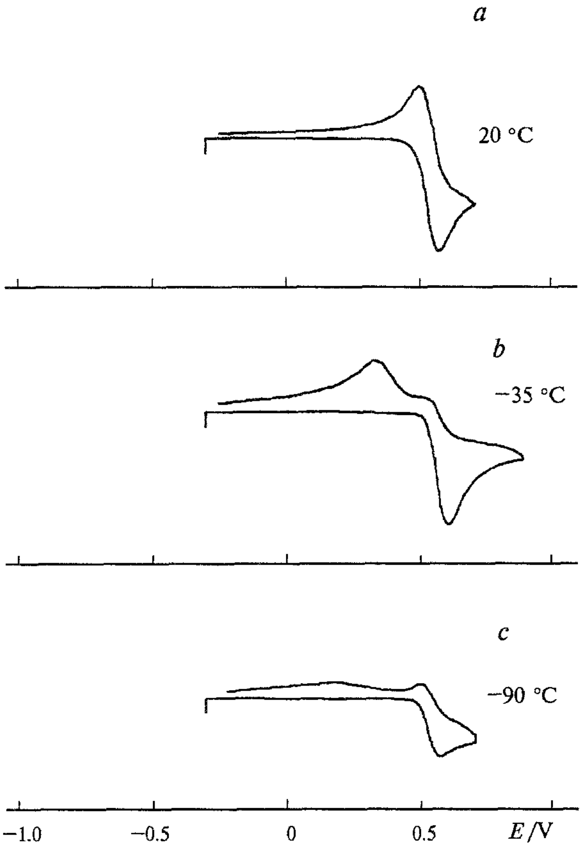


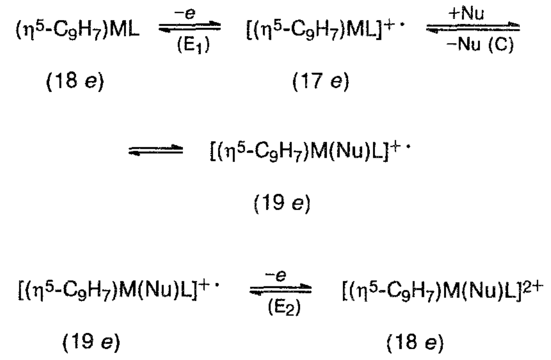
Fig. 3. Cyclic voltammograms of complex **1** (THF/0.05 mol L^{-1} of Bu_4NPF_6) at different temperatures.

reactivity of MeCN can be associated with a small size of its molecule.

Diffusionally controlled two-electron anodic peaks are observed on the cyclic voltammograms of complexes **1**—**3** on a Pt electrode both in THF and MeCN. However, unlike MeCN, the two-electron oxidation of the complexes studied in THF at room temperature occurs reversibly. This follows from the corresponding equal cathodic responses (ΔE_p = 60 to 80 mV, $I_p^a/I_p^c = 1$, 20 °C) on the cyclic voltammograms (Fig. 3, *a*, see Table 1). A decrease in the temperature results in a decrease in the height of the cathodic response, and only an irreversible anodic two-electron peak is observed on the cyclic voltammograms at $T = -30$ to -20 °C. In addition, a decrease in the temperature results in the appearance of a cathodic peak at more negative potentials, which is similar to that observed in MeCN (Fig. 3, *b*). At lower temperatures, this peak nearly disappears, the height of the anodic peak decreases to that of the one-electron peak, and the oxidation becomes reversible (ΔE_p = 40 mV at −70 °C). This follows from the appearance of anodic and cathodic responses of equal heights on the voltammograms (Fig. 3, *c*).

The data obtained altogether show that the one-electron oxidation of compounds **1**—**3** in THF (electrochemical stage E_1, Scheme 2) is followed by the fast reversible chemical reaction (stage C) with the formation of an electroreactive intermediate that is oxidized (stage E_2) easier than the initial complex (process E_1CE_2, $E^o{}_1 > E^o{}_2$). The reversible and fast character of the chemical stage follows from the reversibility of the two-electron oxidation at room temperature. The comparison of the cyclic voltammograms of complexes **1**—**3** in CH_2Cl_2 and THF allows one to draw a conclusion that the chemical stage is the fast reversible reaction of electrogenerated 17-electron radical cations with the solvent (Nu = THF), which results in the formation of 19-electron radical cations $[(\eta^5\text{-}C_9H_7)M(Nu)L]^{+\cdot}$ oxidizable at less positive potentials to form the corresponding 18-electron dications.

Scheme 2



$$\underset{(18\,e)}{(\eta^5\text{-}C_9H_7)ML} \underset{(E_1)}{\xrightleftharpoons{-e}} \underset{(17\,e)}{[(\eta^5\text{-}C_9H_7)ML]^{+\cdot}} \underset{-Nu\ (C)}{\xrightleftharpoons{+Nu}}$$

$$\rightleftharpoons \underset{(19\,e)}{[(\eta^5\text{-}C_9H_7)M(Nu)L]^{+\cdot}}$$

$$\underset{(19\,e)}{[(\eta^5\text{-}C_9H_7)M(Nu)L]^{+\cdot}} \underset{(E_2)}{\xrightleftharpoons{-e}} \underset{(18\,e)}{[(\eta^5\text{-}C_9H_7)M(Nu)L]^{2+}}$$

The temperature decrease reduces abruptly the rate of the reverse chemical reaction (C stage; see Scheme 2), which results in the disappearance of the cathodic response on the voltammograms at $T = -30$ to -20 °C, while the overall two-electron character of the oxidation retains (see Fig. 3, *b*). The subsequent decrease in the temperature is accompanied by the reduction of the rate of the direct chemical reaction of the C stage. As a result, the reversible one-electron oxidation of complexes **1**—**3** is observed at $T < -70$ °C in THF (see Fig. 3, *b*) and at room temperature in CH_2Cl_2 (see Fig. 1, *a*).

The difference observed in the behavior of complexes **1**—**3** in THF and CH_2Cl_2 is caused by the difference in nucleophilic properties of these solvents. Nucleophilic THF is more prone to react with electrogenerated 17-electron radical cations $\mathbf{1}^{+\cdot}$—$\mathbf{3}^{+\cdot}$ than CH_2Cl_2, and this reaction is reversible due to the comparatively weak nucleophilic properties of THF. The reaction of radical cations with stronger nucleophiles should shift the equilibrium of the C stage to the formation of the 19-electron adduct and should result in the irreversible two-electron oxidation of the complexes, which is observed in the case of MeCN (see above). A similar situation takes place when Cl^- anions (in the form of Et_3PhCH_2NCl)

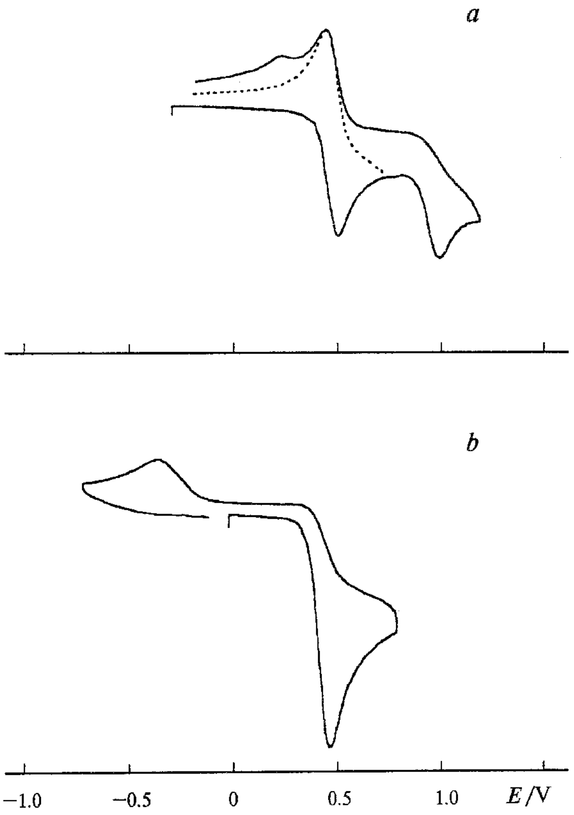


Fig. 4. Cyclic voltammograms of complex **4** in THF/0.1 mol L^{-1} of Bu_4NPF_6 (*a*) and MeCN/0.1 mol L^{-1} Bu_4NPF_6 (*b*).

are added to a CH_2Cl_2 solution of the complexes under study. For example, the anodic peak of the oxidation of complex **1** becomes irreversible and two-electron, and a peak ($E_p^c = -0.65$ V) that evidently corresponds to the reduction of an 18-electron complex $[(\eta^5\text{-}C_9H_7)_2RuCl]^+$ formed is observed on the cathodic branch of the cyclic voltammogram (see Fig. 1, *b*).

Unlike complexes **1**—**3**, the oxidation of osmium bis-indenyl complex **4** in THF is reversible and one-electron (Fig. 4, *a*) even at room temperature, *i.e.*, radical cation $\mathbf{4}^{+\cdot}$ is more inert toward the reaction with THF, although it reacts with relatively strong nucleophiles, MeCN or Cl^-, like complexes $\mathbf{1}^{+\cdot}$—$\mathbf{3}^{+\cdot}$ (Fig. 4, *b*). The preparative one-electron oxidation of **4** (electrochemical or chemical oxidation under the action of $AgBF_4$) results in the formation of a brown solution, which is comparatively stable in an argon atmosphere and whose ESR spectrum exhibits only one signal with $g = 2.003$.

It is known that the chemical oxidation of ruthenocene and osmocene in the presence of strong nucleophiles results in the formation of cationic complexes $(\eta^5\text{-}C_5H_5)_2MX^{n+}$ (M = Ru, Os, X = Cl, Br, I, $n = 1$; M = Os, X = MeCN, $n = 2$)[9—11] with the bent sandwich structure.[12] It can be supposed by analogy that electrogenerated Ru^{IV} and Os^{IV} indenyl complexes and the corresponding 19-electron radical cations also have the bent sandwich structure.

Thus, the reactions of ruthenium and osmium 17-electron radical cation indenyl complexes with nucleophiles resulting in the formation of 19-electron radical cations (or radicals in the case of Nu = X^-) facilitate considerably the elimination of an unpaired electron to form 18-electron dications (or cations) stabilized by the electron pair of the nucleophile.

The comparison of the potentials of the one-electron oxidation of sandwich complexes **1**—**3** as well as of $(\eta^5\text{-}C_5H_5)_2Ru$, $(\eta^5\text{-}C_9H_7)_2Ru$, and $(\eta^5\text{-}C_5Me_5)_2Ru$ (see Table 1) and the kinetic stability of the corresponding electrogenerated 17-electron radical cations (whose criterion is the degree of reversibility and the electronic character of the oxidation of the initial complexes in the presence of nucleophiles) make it possible to draw a conclusion that the reactivity of radical cations in the nucleophilic addition reactions depends on the nature of the ligand and increases in the following series $[(\eta^5\text{-}C_9H_7)Ru(\eta^5\text{-}C_5Me_5)]^{+\cdot} < [(\eta^5\text{-}C_9H_7)Ru(\eta^5\text{-}C_9H_7)]^{+\cdot} < [(\eta^5\text{-}C_9H_7)Ru(\eta^5\text{-}C_5H_5)]^{+\cdot}$ and $[(\eta^5\text{-}C_5Me_5)_2Ru]^{+\cdot} < [(\eta^5\text{-}C_9H_7)_2Ru]^{+\cdot} < [(\eta^5\text{-}C_5H_5)_2Ru]^{+\cdot}$ in parallel with an increase in donor properties of the π-ligand[6] $\eta^5\text{-}C_5Me_5 > \eta^5\text{-}C_9H_7 > \eta^5\text{-}C_5H_5$.

It follows from the data obtained that ruthenium cyclopentadienyl complexes should manifest the maximum activity in reactions with nucleophiles. In accordance with this, the reversible one-electron oxidation of $(C_5H_5)_2Ru$ was observed only in an $AlCl_3$/1-butylpyridinium chloride melt,[13] while in THF and MeCN the oxidation occurs as one irreversible two-electron stage according to the ECE scheme.[1,14] It is evident that in this case the C stage is also the reaction of the electrogenerated 17-electron ruthenocene radical cation with the nucleophile with the formation of an easier oxidizable 19-electron intermediate. It should be mentioned that the nature of the C stage of the electrochemical oxidation of ruthenocene has been unclear yet.[15]

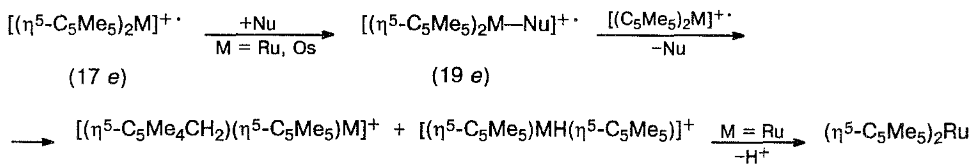
The results obtained in the present work allow one to suppose the formation of 19-electron intermediates in chemical reactions of 17-electron radical cations of ruthenium and osmium sandwich complexes occurring in the absence of nucleophiles. One of these reactions is the disproportionation of $\mathbf{1}^{+\cdot}$ electrochemically generated in a CH_2Cl_2 solution under the action of Cl^- with the formation of **1** and $[(\eta^5\text{-}C_9H_7)_2RuCl]^+$, that has been observed in the present work (Scheme 3).

Scheme 3

$$[(\eta^5\text{-}C_9H_7)_2Ru]^{+\cdot} \xrightarrow[CH_2Cl_2]{+Cl^-} [(\eta^5\text{-}C_9H_7)Ru\text{—}Cl]^{\cdot} \longrightarrow$$

$$\xrightarrow{[(\eta^5\text{-}C_9H_7)_2Ru]^{+\cdot}} (\eta^5\text{-}C_9H_7)_2Ru + [(\eta^5\text{-}C_9H_7)_2Ru\text{—}Cl]$$

Scheme 4



$$[(\eta^5\text{-}C_5Me_5)_2M]^{+\cdot} \xrightarrow[M\,=\,Ru,\,Os]{+Nu} [(\eta^5\text{-}C_5Me_5)_2M{-}Nu]^{+\cdot} \xrightarrow[-Nu]{[(C_5Me_5)_2M]^{+\cdot}}$$

$$(17\ e) \qquad (19\ e)$$

$$\longrightarrow [(\eta^5\text{-}C_5Me_4CH_2)(\eta^5\text{-}C_5Me_5)M]^{+} + [(\eta^5\text{-}C_5Me_5)MH(\eta^5\text{-}C_5Me_5)]^{+} \xrightarrow[-H^+]{M\,=\,Ru} (\eta^5\text{-}C_5Me_5)_2Ru$$

It is likely that the disproportionation reactions of 17-electron osmium cyclopentadienyl complexes described previously[11] also occur with the formation of 19-electron intermediates.

In the case of 17-electron permethylated osmium and ruthenium complexes, the C—H bond of the methyl group is involved in the reaction,[16] which results in the transfer of an H atom (Scheme 4).

Decamethylruthenocene is a weaker base than the osmium analog,[17] therefore, its protonated form easily looses a proton, and only decamethylruthenocene is observed in the reaction products.

The participation of the nucleophile in this process is not evident, because it is not incorporated into the final products. However, it has been shown in the present work with decamethylruthenocene as an example that the transfer of an H atom (see Scheme 4) is promoted by the catalytic amount of Cl^-. The addition of the catalytic amount of Cl^- (the ratio $Et_3PhCH_2NCl/[(C_5Me_5)_2Ru]^{+\cdot} = 0.1$ to 0.2) to a solution of $[(C_5Me_5)_2Ru]BF_4$ in CH_2Cl_2 results in almost instantaneous disappearance of the peak of the reduction of decamethylruthenocenium and the appearance of the peak of the oxidation of $(\eta^5\text{-}C_5Me_5)_2Ru$ and a new peak with the equal height, although the peaks on the cyclic voltammogram were unchanged for several hours in the absence of Cl^-. The latter new peak corresponds to the reduction of the $[(\eta^5\text{-}C_5Me_4CH_2)(\eta^5\text{-}C_5Me_5)Ru]^+$ complex identified by comparison with the peak of the identical sample. Thus, the results obtained allow one to suppose that the hydrogen transfer (see Scheme 4) occurs in the catalytic regime involving the 19-electron intermediate formed upon the addition of the nucleophile. It is noteworthy that these reactions have been previously considered either without taking into account the stage of the reaction of 17-electron radical cations with nucleophiles[16] or not occurring in the catalytic regime.[9] It is highly probable that the previously observed reaction of the H atom transfer for radical cation $3^{+\cdot}$ resulting in the formation of $[(\eta^5\text{-}C_9H_7)(\eta^5\text{-}C_5Me_4CH_2)Ru]^+$ and $[(\eta^6\text{-}C_9H_8)(\eta^5\text{-}C_5Me_5)Ru]^+$ cationic complexes[18] also involves 19-electron intermediates.

The ability of ruthenium and osmium 17-electron radical cation sandwich complexes to transform into 19-electron complexes under the action of nucleophiles demonstrated in the present work is one of the most important properties of electron-deficient odd-electron species. The specific feature of the complexes studied in our work is the fact that 17-electron complexes transform into 19-electron complexes under the action of even relatively weak nucleophiles such as THF.

Experimental

Electrochemical measurements were performed on a PAR-173 potentiostat. A custom-made cell containing a 1-mm disk working Pt electrode, an Ag/AgCl reference electrode, and a Pt-wire as an accessory electrode was used for low-temperature electrochemical measurements. The reference electrode was connected with the main solution by a salt bridge filled with a solution of a base electrolyte and provided with a graphite membrane sealed into the glass. The temperature of the reference electrode was ~20 °C in the course of low-temperature measurements. All potentials were measured relative to a saturated calomel electrode and were compared with the potentials of the Cp_2Fe/Cp_2Fe^+ or $Cp^*{}_2Fe/Cp^*{}_2Fe^+$ (Cp^* is pentamethylcyclopentadienyl) couples, which were +0.43, +0.44, +0.42 and −0.10, −0.00, −0.08 V relative to a saturated calomel electrode in CH_2Cl_2, THF, and MeCN, respectively. Controlled potential electrolysis was carried out on a P-5827M potentiostat and on an OH-404 digital coulometer (Radelkis) in a cylindrical cell with anodic and cathodic spaces separated by a porous glass diaphragm. The surface of the foil Pt-electrode was 35 cm^2.

NMR and ESR spectra were recorded on Bruker WP 200SY and Varian 12 spectrometers, respectively.

All procedures were carried out in an argon atmosphere. CH_2Cl_2 was purified by the known procedure[19] and kept in argon in dark at 0 °C. THF was distilled over sodium benzophenone ketyl prior to use. MeCN was purified by the procedure described previously,[20] kept over CaH_2, and distilled prior to use. Bu_4NPF_6 (Fluka) or Bu_4NBF_4 (Fluka) were used as base electrolytes and dried by melting *in vacuo* before distillation of a solvent. A purified solvent (CH_2Cl_2, MeCN, or THF) was distilled in argon into a special buret with the base electrolyte and then was placed without contact with air into an electrochemical cell preliminarily dried *in vacuo* and filled with argon. These procedures excluded the presence of traces of air and water in the solution studied. Complex **1** was synthesized by the known procedure.[21] Complexes **2** and **3** were synthesized in the reaction of indenyllithium with $[(\eta^5\text{-}C_5R_5)Ru(MeCN)_3]^+PF_6^-$ (R = H, Me) or $[(\eta^5\text{-}C_5Me_5)RuCl_2]_x$.[22]

$(\eta^5\text{-}C_9H_7)_2Os$. Zinc dust (3 g) was added portionwise to a mixture of $(Bu_4N)_2OsCl_3$ (2.2 g, 2.48 mmol) and indene (6 mL) in 100 mL of MeOH/EtOH (1 : 1). The reaction mixture was stirred for 0.5 h at ~20 °C and for 2 h at 45 °C and then was refluxed for 4 h. After cooling, the solvent was evaporated, and the residue was extracted with a 1 : 1 petroleum ether—benzene mixture. The product obtained after evaporation of the solvent was washed with a cold 1 : 1 Me_2CO—EtOH mixture. Crystals were filtered off, dissolved in

CH_2Cl_2, and precipitated with ether. Recrystallization from $MeOH/Me_2CO$ (4 : 1) yielded 86 mg (yield 11 %) of complex **4** as golden crystals. Found (%): C, 51.51; H, 3.42; Os, 45.58. $C_{18}H_{14}Os$. Calculated (%): C, 51.41; H, 3.36; Os, 45.23. ^1H NMR, δ: 4.84 (t, 1 H_b, J = 1.8 Hz); 5.15 (d, 2 H_a, J = 2.2 Hz); 6.42—6.47 (t, 2 α-H (β-H)); 6.57—6.62 (t, 2 β-H (α-H)).

$[(\eta^5\text{-}C_5Me_5)Ru]^+BF_4^-$. Thoroughly dried $AgBF_4$ (0.1 g, 0.51 mmol) was dissolved in CH_2Cl_2 (10 mL) and added to a solution of of $(\eta^5\text{-}C_5Me_5)_2Ru$ (0.185 g, 0.50 mmol) in 20 mL of CH_2Cl_2. A red solution obtained was filtered and concentrated to 5 mL, and 100 mL of absolute ether was added to the filtrate. A pink finely crystalline residue was filtered off and reprecipitated from a CH_2Cl_2/ether mixture. The complex $[(\eta^5\text{-}C_5Me_5)_2Ru]^+BF_4^-$ (0.16 g, 70 %) was obtained.

References

1. V. V. Strelets, *Coord. Chem. Rev.*, 1992, **114**, 1.
2. L. I. Denisovich, M. G. Peterleitner, D. N. Kravtsov, A. Z. Kreindlin, S. S. Fadeeva, and M. I. Rybinskaya, *Metalloorg. Khim.*, 1989, **2**, 301 [*Organomet. Chem. USSR*, 1989, **2** (Engl. Transl.)].
3. P. M. Treichel, J. W. Johnson, and K. P. Wagner, *J. Organomet. Chem.*, 1975, **88**, 227.
4. S. V. Kukharenko, V. V. Strelets, N. A. Ustynyuk, L. N. Novikova, M. G. Peterleitner, and L. I. Denisovich, *Metalloorg. Khim.*, 1991, **4**, 299 [*Organomet. Chem. USSR*, 1991, **4** (Engl. Transl.)].
5. L. N. Novikova, N. A. Ustynyuk, L. I. Denisovich, M. G. Peterleitner, S. V. Kukharenko, V. V. Strelets, and Yu. F. Oprunenko, *Metalloorg. Khim.*, 1991, **4**, 871 [*Organomet. Chem. USSR*, 1991, **4** (Engl. Transl.)].
6. P. G. Gassman and C. H. Winter, *J. Am. Chem. Soc.*, 1988, **110**, 6130.
7. V. Gutman, *Coordination Chemistry in Non-Aqueous Solutions*, Springer-Verlag, Vienna—New York, 1968.
8. Y. Zhang, D. K. Gosser, P. H. Reiger, and D. A. Sweigart, *J. Am. Chem. Soc.*, 1991, **113**, 4062.
9. U. Koelle, *J. Organomet. Chem.*, 1985, **289**, 133.
10. T. P. Smith, K. S. Kwan, H. Taube, A. Bino, and S. Cohen, *Inorg. Chem.*, 1984, **23**, 1943.
11. M. W. Droege, W. D. Harman, and H. Taube, *Inorg. Chem.*, 1987, **26**, 1309.
12. T. P. Smith, D. J. Iverson, M. W. Droege, K. S. Kwan, and H. Taube, *Inorg. Chem.*, 1987, **26**, 2882.
13. R. J. Gale and R. Job, *Inorg. Chem.*, 1981, **20**, 42.
14. M. G. Hill, W. M. Lamanna, and K. R. Mann, *Inorg. Chem.*, 1992, **30**, 4687.
15. S. V. Kukharenko, A. A. Bezrukova, A. Z. Rubezhov, and V. V. Strelets, *Metalloorg. Khim.*, 1990, **3**, 634 [*Organomet. Chem. USSR*, 1990, **3** (Engl. Transl.)].
16. M. I. Rybinskaya, A. Z. Kreindlin, and S. S. Fadeeva, *J. Organomet. Chem.*, 1988, **358**, 363.
17. L. M. Epshtein and E. S. Shubina, *Metalloorg. Khim.*, 1992, **5**, 61 [*Organomet. Chem. USSR*, 1992, **5** (Engl. Transl.)].
18. A. Z. Kreindlin, P. V. Petrovskii, and M. I. Rybinskaya, *Metalloorg. Khim.*, 1991, **4**, 63 [*Organomet. Chem. USSR*, 1991, **4** (Engl. Transl.)].
19. J. Heinze, *J. Am. Chem. Soc.*, 1990, **112**, 5142.
20. J. F. O'Donnel, J. T. Ayres, and C. K. Mann, *Anal. Chem.*, 1961, **37**, 1161.
21. N. S. Grossley, J. C. Green, and G. Stringer, *J. Chem. Soc., Dalton Trans.*, 1989, 2139.
22. A. R. Kudinov and M. I. Rybinskaya, *Metalloorg. Khim.*, 1988, **1**, 1429 [*Organomet. Chem. USSR*, 1988, **1** (Engl. Transl.)].

Received April 27, 1995