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CHEMICAL AND ELECTROCHEMICAL OXIDATION OF METALLOCENES. REACTIONS OF METALLOCENES WITH MERCURY SALTS

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Summary

The products of chemical and electrochemical oxidation of metallocenes, $(C_5H_5)_2M$ (M = Fe, Ru, Os), were investigated. $(C_5H_5)_2Fe$ on Pt and Hg anodes was oxidized to the ferricenium cation while the electrolysis of osmocene on Pt electrode led to the previously unknown $(C_5H_5)_2Os^+BF_4^-$ salt and oxidation of ruthenocene yielded the unstable $(C_5H_5)_2Ru^{2+}$ cation. On a mercury electrode Ru and Os metallocenes gave the adducts $[(C_5H_5)_2M]_2Hg(BF_4)_2$. The stability constants of mercury-containing complexes were calculated using the polarographic data. The chemical interaction of metallocenes with HgX_2 also gave mercury-containing adducts. Chemical oxidation of ruthenocene resulted in salts with the metal in the +4 formal oxidation state.

Among the oxidation products of the iron group metallocenes only ferricenium salts have been thoroughly investigated. Synthetic methods have been proposed [1]. The physical and chemical properties and the structures of such compounds have been studied by means of ESR [2], NMR [3], IR [4], UV [5] and X-ray spectroscopy [6]. Unlike ferricenium salts the respective osmicenium and ruthenicenium salts are practically unknown. Soft oxidizing agents such as $AgNO_3$ and *p*-quinone which oxidize ferrocene to $(C_5H_5)_2Fe^+$ do not act on osmocene, while stronger oxidizing agents ($KMnO_4$, Cl_2) decompose the osmocene molecule. Only oxidation of osmocene with iodine in acid is known to give $(C_5H_5)_2OsI^+PF_6^-$ with some impurity, and oxidation with acidic aqueous Fe^{3+} afforded a diamagnetic salt, $(C_5H_5)_2OsOH^+PF_6^-$ [7]. The formal osmium oxidation state in these compounds is +4. Analogously to ferrocene, ruthenocene has been oxidized with bromine water and Ag_2SO_4 [8], but the products were not specified. Only ruthenicemium triiodide has been reported; it precipitated as a red solid on mixing the iodine and ruthenocene solutions in CCl_4 or benzene [9]. As with osmocene, stronger oxidizing agents decompose the ruthenocene molecule into Ru^{III} and Ru^{IV} salts.

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Electrochemical oxidation of the iron subgroup metallocenes has been studied in a number of works [10—13]. It has been shown [12,13] that on a Pt electrode ruthenocene was oxidized to $(C_5H_5)_2Ru^{2+}$ and osmocene was oxidized stepwise via two electrochemically irreversible one-electron steps, but the products were not isolated. The electrolysis of ferrocene on Hg and Pt anodes at a controlled potential led to blue ferricenium salt solutions [14,15]. Electrolysis of ruthenocene on an Hg anode afforded a yellow substance with a salt-like structure, $(C_5H_5)_2Ru^+ClO_4^-$ [8]. However a later careful analysis of the product of the electrolysis of ruthenocene in 90% C_2H_5OH with 0.1 *N* $NaClO_4$ showed [16] that it was a diamagnetic complex, $[(C_5H_5)_2Ru]_2Hg^{2+}(ClO_4)_2^-$. Moreover, ruthenocene and ferrocene reacted chemically with the mercury salts $HgCl_2$ and $HgBr_2$, giving the adducts $(C_5H_5)_2Ru \cdot HgX_2$, $(C_5H_5)_2Ru \cdot 3HgCl_2$, $(C_5H_5)_2Ru \cdot 1.8HgBr_2$ and $(C_5H_5)_2Fe \cdot 7HgCl_2$, depending on the ratio of reagents. Thus we thought it worthwhile to study the possibility of electrochemical synthesis of ruthenocene and osmocene salts and to analyze their chemical and electrochemical oxidation and the ability of metallocenes to produce complexes with mercury salts. Electrochemical investigations were carried out on Hg and Pt electrodes in anhydrous CH_3CN in the presence of R_4NBF_4 (R = Et, Bu).

Results

Electrochemical oxidation of ferrocene

One anodic wave corresponding to a reversible one-electron process (Table 1) was observed in the ferrocene polarogram on a DME (dropping mercury electrode) and a rotating disc Pt electrode. The half-wave potential $E_{1/2}$ is independent of ferrocene concentration. The close $E_{1/2}$ values of the waves on DME and Pt electrodes (Table 1) show that ferrocene oxidation is not due to an electrode material and a possibility of formation of mercury-containing ferrocene products on the Hg electrode is excluded. Actually the electrolysis on the Pt electrode at a controlled potential or a stirring mercury anode gives blue ferricenium salt solutions. In the course of electrolysis the anodic wave of ferrocene slowly transforms to an anode—cathodic one and then to a cathodic wave of ferricenium ions. The half-wave potentials of these waves coincide within the accuracy of potential measurements. Thus ferrocene oxidation on either Hg or Pt electrodes affords the same product, the ferricenium cation.

Anodic behaviour of ruthenocene and osmocene on a DME

The number of waves in polarograms of ruthenocene and osmocene on Pt and DME and wave characteristics are different [13], which may mean that there is participation of electrode material in the electrochemical reaction. The polarograms of $(C_5H_5)_2M$ (M = Ru, Os) on a DME show one anodic wave. The measurements on Kalousek switch [13] manifested the electrochemical reversibility of the process. Electrolysis at the limiting current potential of this wave on rotating mercury anode converted primarily colourless solutions into yellow ones. The anodic waves became gradually anode—cathodic and then cathodic. However, the compounds isolated from the solutions were not metallicenium salts, $(C_5H_5)_2M^+$ (M = Ru, Os), but their IR and UV spectra and polarographic data

TABLE 1

POLAROGRAPHIC CHARACTERISTICS OF FERROCENE, RUTHENOCENE, OSMOCENE AND THEIR DERIVATIVES

($C = 1 \times 10^{-3}$ mol l^{-1}, CH_3CN, 0.1 *N* Bu_4NBF_4, versus $Ag/AgClO_4$, 0.01 *N* in 0.1 *N* Et_4NClO_4)

Compound	DME				Pt electrode			
	$E_{1/2}$ (V)	i (μA)	Triangular voltammetry		$E_{1/2}$ (V)	i (μA)	Triangular voltammetry	
			$E_{p.a.}$	$E_{p.c.}$			$E_{p.a.}$	$E_{p.c.}$
$(C_5H_5)_2Fe$	0.12	3.40	0.15^b	0.08	0.13^d	11	0.18	0.11
$(C_5H_5)_2Ru$	0.06	3.30	0.09^b	0.03	0.60^d	20	0.64	
$(C_5H_5)_2Os$	−0.15	3.20	−0.16^b	−0.11	0.48^d	11	0.55	
					1.52^d	5.0		
$[(C_5H_5)_2Ru]_2Hg(BF_4)_2$	0.05	4.20	0.08^c	0.02	−0.12^a	13		−0.27
$[(C_5H_5)_2Os]_2Hg(BF_4)_2$	−0.18	4.60	−0.17^c	−0.12	−0.20^a	14		−0.38
$(C_5H_5)_2FeBF_4$					0.14^a	5.6		
$[(C_5H_5)RuCl]FeCl_4$					−0.03^a	10		
					−0.29^a	10		

^{a} Cathodic wave. ^{b} Anodic polarization. ^{c} Cathodic polarization. ^{d} Anodic wave.

were similar to those of $[(C_5H_5)_2M]_2Hg(BF_4)_2$ prepared by chemical reaction of $(C_5H_5)_2M$ with $Hg(CN)_2$ in the presence of HBF_4. The polarogram of $[(C_5H_5)_2M]_2Hg(BF_4)_2$ contains one cathodic wave whose investigation sheds light on the nature of processes occurring in anodic depolarization of $(C_5H_5)_2M$. Thus measurements on Kalousek switch and a comparison of wave heights for $[(C_5H_5)_2M]_2Hg(BF_4)_2$ and $(C_5H_5)_2M$ demonstrates reversible two-electron reduction of $[(C_5H_5)_2M]_2Hg(BF_4)_2$. Wave pattern analysis for $[(C_5H_5)_2M]_2Hg(BF_4)_2$ employing eqn.1 derived for the reversible reduction of mercury complexes on DME [18] showed that the plot of log $i^2/(i_d - i)$ vs E is linear with a slope of 32 mv, close to the theoretical value. The data obtained and the virtual coincidence of $E_{1/2}$'s of the reversible two-electron reduction of $[(C_5H_5)_2M]_2Hg(BF_4)_2$ and anodic wave of $(C_5H_5)_2M$, and a coincidence of $E_{p.a.}$ and $E_{p.c.}$ on oscillopolarograms (Table 1) indicate that the reduction of $[(C_5H_5)_2M]_2Hg(BF_4)_2$ follows eqn.2, which demonstrates that the waves observed on polarograms of $(C_5H_5)_2M$ on DME correspond to the dissolution of anodic mercury and formation of mercury-containing complexes, not $(C_5H_5)_2M^+$ cations, as previously suggested [8,13].

$$E = E^0_{Hg/Hg^{2+}} - \frac{RT}{2F} [\ \ln \frac{i^2}{i_d - i} - \ln \frac{\chi_2}{\chi_0^2} - \ln k_2\ ] \qquad (1)$$

(where $E^0_{Hg/Hg^{2+}}$ is the normal Hg/Hg^{2+} potential; $k_2 = [[(C_5H_5)_2M]_2Hg^{2+}]/[Hg^{2+}][(C_5H_5)_2M]^2$ is the total stability constant of reduced complex; χ_2 and χ_0 are the coefficients of Il'kovich equation for $[(C_5H_5)_2M]_2Hg^{2+}$ and $(C_5H_5)_2M$ respectively)

$$[(C_5H_5)_2M]_2Hg^{2+} + 2e^- \rightleftharpoons Hg^0 + 2(C_5H_5)_2M \qquad (2)$$

$$E = E^0_{Hg/Hg^{2+}} - \frac{RT}{2F}\left[\ln k_2 + \ln \frac{X_0^2}{X_2} + \ln \frac{i}{(i_d - i)^2} \right] \qquad (3)$$

Hence process 2 is reversible electrochemically and the form of anodic wav of $(C_5H_5)_2M$ obeys eqn.3 [18,19]: The plot of log $i/(i_d - i)^2$ vs E is linear for $(C_5H_5)_2M$ (M = Ru, Os), with slopes equal to 37 and 39 mV, and at a 10-fold increase of concentration the half-wave potentials are shifted by 30 and 33 mV respectively to negative. These values are close to the theoretical ones which confirms validity of eqn.2. Computation of k_2 values using eqn.1 and eqn.3 gave $10^{11.2}$ for $[(C_5H_5)_2Ru]_2Hg(BF_4)_2$ and $10^{19.5}$ (mol^{-1}) for $[(C_5H_5)_2Os]_2Hg(BF_4)_2$. The stability constant of mercury-containing complex of osmocene is higher than that of the ruthenocene complex, in good agreement with our chemical data on metallocene ability to produce adduct with HgX_2 (details will be discussed below).

Oxidation of ruthenocene and osmocene on a Pt electrode

Oxidation of ruthenocene on a Pt electrode involves the removal of two electrons [13]. Chronopotentiometry [12] and triangular voltammetry data (Table 1) manifest the electrochemical irreversibility of the process. However, our attempts to isolate $(C_5H_5)_2Ru^{2+}$ by electrolysis of ruthenocene on the Pt electrode in CH_3CN in the presence of Et_4NBF_4 were unsuccessful. Probably $(C_5H_5)_2Ru^{2+}$, generated at first as an oxidation product, decomposes into ruthenium salts. On the other hand, chemical oxidation of ruthenocene with $FeCl_3$ in ether and with Br_2 in benzene yielded the salts $[(C_5H_5)_2RuCl]FeCl_4$ and $[(C_5H_5)_2RuBr]Br_3$. The presence of $FeCl_4^-$ anion in the first salt was confirmed by Mössbauer spectra and polarography (Table 1). Apparently the presence of anions Cl^- and Br^- in the inner coordination sphere stabilizes the formally +4 ruthenium oxidation state in this molecule. It is quite probable that the absence of an anion acting in such manner in the electrolyzed solution results in decomposition of the primarily-generated $(C_5H_5)_2Ru^{2+}$.

Oxidation of osmocene on the Pt electrode has two steps, the first being one-electron*. Chronopotentiometry [12,20] and triangular voltammetry ($I_{p.c.}/I_{p.a.} \neq 1$) data reveal the electrochemical irreversibility of the process. Electrolysis at the limiting current potential of this wave leads to a dark green salt, $(C_5H_5)_2OsBF_4$, insoluble in CH_3CN, whose structure and composition were confirmed by elemental analysis and IR spectra. At the present time it is the only osmicenium salt with osmium in the formal +3 oxidation state. Reduction of its aqueous solution with acidified $SnCl_2$ solution leads to osmocene. Low solubility of this salt in organic solvents prevent its investigation with other chemical and physico-chemical methods.

Metallocene complexes with HgX_2 (X = Cl, Br)

It was shown that the reaction of $HgCl_2$ with excess ferrocene gives an unstable red complex, $(C_5H_5)_2Fe \cdot 6HgCl_2$**. The $HgCl_2$ of the complex is reduced on standing for a while and the ferrocene is oxidized to the ferricenium cation.

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* Electrolysis at the limiting current potential of the second oxidation of osmocene was not performed in the present work.

** An excess of $HgCl_2$ gives the complex $(C_5H_5)_2Fe \cdot 7HgCl_2$ [17].

When alcohol solutions of ruthenocene and osmocene are mixed with HgX_2, instant precipitation of yellow crystalline substances is observed. They crystallize from CH_3CN* and are stable in air and poorly soluble in a majority of organic solvents. Elemental analyses favour 1/1 composition. Substituted metallocenes also produce complexes with $HgCl_2$ [e.g. $(C_5H_5)Ru(C_5H_4HgCl)$, $(C_5H_5)Ru(C_5H_4COCH_3)$, $(C_5H_5)Ru(C_5H_4B(OH)_2)$]. Acetylruthenocene gives the complex $(C_5H_5)Ru(C_5H_4COCH_3)\cdot 2HgCl_2$. The IR spectrum of this compound has an unchanged CO vibration band at 1680 cm^{-1}.

The PMR spectrum of complex $(C_5H_5)_2Ru\cdot HgCl_2$ in methanol shows a narrow signal at 4.57 ppm corresponding to 10 equivalent C_5H_5 protons. The UV spectrum of this complex in CH_3CN exhibits an intense band at 280 nm which is absent from ruthenocene spectrum.

The structure of $(C_5H_5)_2Ru\cdot HgBr_2$ was established by X-ray analysis [21]. The molecules are associated into dimers via bromine bridges. The length of Ru—Hg bond is 2.74 Å. For comparing the reactivities of metallocenes at the formation of the complexes with $HgCl_2$ the authors have studied the competitive reactions of metallocene with $HgCl_2$ and exchange reactions of metallocenes in the $HgCl_2$ complexes. It was shown that an addition of $HgCl_2$ to an equimolar mixture of $(C_5H_5)_2Fe$ and $(C_5H_5)_2Ru$ leads to 65% of only the ruthenocene—$HgCl_2$ complex. On addition of $HgCl_2$ to a benzene—alcohol solution (3/1) of equimolar amounts of $(C_5H_5)_2Ru$ and $(C_5H_5)_2Os$, the complex of $(C_5H_5)_2Os$ with $HgCl_2$ is formed in triple excess with respect to $(C_5H_5)_2Ru\cdot HgCl_2$. Investigation of the exchange reactions of metallocenes in $HgCl_2$ complexes demonstrated that heating of $(C_5H_5)_2Ru\cdot HgCl_2$ for 10 min in CH_3CN in the presence of equimolar osmocene quantity afforded the complex $(C_5H_5)_2Os\cdot HgCl_2$. These results indicate that among the three metallocenes investigated osmocene forms the most stable and least soluble complexes with $HgCl_2$.

Discussion

The results obtained in the present study show that the change of redox properties of the iron subgroup metallocenes is abrupt on going from ferrocene to ruthenocene and osmocene, and the latter two compounds have similar properties, but which are considerably different from those of ferrocene. Thus ferrocene is electrochemically oxidized reversibly on DME to the ferricenium cation, while ruthenocene and osmocene produce complexes with Hg^{2+} ions due to anodic dissolution of mercury. The oxidation on a Pt electrode of these metallocenes is also different. Ferrocene is reversibly oxidized to ferricenium whereas ruthenocene and osmocene are oxidized irreversibly with loss of two electrons. The reason for the irreversibility in the case of ruthenocene may be a hindered electrochemical reaction, since the structures of initial depolarizator, ruthenocene, and the primary product, $[(C_5H_5)_2Ru]^{2+}$ should be essentially different. In the case of osmocene one possible reason may be the very low solubility of the resultant salt, $(C_5H_5)_2OsBF_4$.

Chemical oxidation of these metallocenes is also different. We have mentioned in the Introduction that the action of various oxidizing agents on ferro-

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* One may obtain other complexes (e.g. 2/3) by recrystallization of the 1/1 complex, due to the differing solubilities of $(C_5H_5)_2M$ and HgX_2.

cene leads to ferricenium salts, whereas the data of present work show that chemical oxidation of ruthenocene yields ruthenicenium salts with ruthenium in the formal +4 oxidation state (instead of +3 as in ref.8). It follows from these results that an estimation of the relative susceptibility towards oxidation of the metallocenes, either quantitatively (by comparison of half-wave potentials at DME and Pt electrodes) or qualitatively (by comparing the action of the same reagents), is impossible because of different reaction mechanisms of the product generated*. Since oxidation removes an electron from the highest occupied molecular orbital of the complex, the different behaviour of the iron subgroup metallocenes in oxidation should be due to differences in their electronic structures.

Quantum-chemical computations [22] and helium photoelectron spectral data [23,24] indicate that in ferrocene the highest occupied molecular orbital is a doubly-degenerate weakly bonding e_{2g} orbital with nearly 75% contribution of $3d$ iron orbitals (d_{xy}, $d_{x^2-y^2}$). Quantum-chemical calculations on the ferricenium cation [25,26] and magnetic measurements [27] along with ESR spectra [28, 29] show that on going from ferrocene to the ferricenium cation an electron is removed from the e_{2g} orbital, and thus the ground state of ferricenium cation should be $^2E_{2g}(a_{1g})^2(e_{2g})^3$.

At present no quantum-chemical computations have been performed for osmocene and ruthenocene. It has been assumed [30] that on formation of $(C_5H_5)_2M$ (M = Ru, Os) the valent states of metal atoms are the same as in $(C_5H_5)_2Fe$, but the relative MO energies should differ from those of ferrocene due to the change of metal atomic orbital and valence electronic levels in the complexes. Actually the data of helium photoelectronic spectra [23] concerning the upper occupied orbitals indicate that the ionization energies of e_{2g} and a_{1g} orbitals increase appreciably on going from ferrocene [6.88 eV (e_{2g}) and 7.23 eV (a_{1g})] to ruthenocene [7.45 eV (e_{2g}) and 7.63 eV (a_{1g})]. However the average ionization energy of d-electrons in $(CH_3C_5H_4)_2Os$ (7.23 eV) is scarcely different from that of $(CH_3C_5H_4)_2Ru$ (7.25 eV). Moreover it is important to note that the energy difference of e_{2g} and a_{1g} orbitals of ruthenocene is essentially smaller (0.18 eV) than in ferrocene (0.35 eV), and in osmocene an upper occupied orbital may be a_{1g} instead of e_{2g}.

Thus different energies and location of the upper occupied orbitals in metallocenes may cause ruthenocene and osmocene to behave in a different manner in oxidation to ferrocene.

The difference in ruthenocene, osmocene and ferrocene behaviour is pronounced also in the formation of donor—acceptor complexes with a weak Lewis acid such as HgX_2 [31]. Ruthenocene and osmocene produce stable complexes with HgX_2 which have definite composition, while ferrocene gives unstable adducts which readily undergo redox reaction with formation of the ferricenium cation [32]. It should be pointed out that osmocene and ruthenocene complexes with HgX_2 are the only known adducts of these metallocenes, while ferrocene reacts with various acceptors: π-acids [33—37] and Lewis acids. It was found that depending on the properties of an acceptor one may produce adducts (CTC) [38] or perform a redox reaction on the ferricenium cation. Previous workers

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* In the view of these results we have to admit that our previous estimations of ionization potentials carried out for ruthenocene and osmocene [13] (but not for other metallocenes) are erroneous.

[36] have failed to prepare CTC by reaction of ruthenocene and osmocene with tetracyanoethylene, while HgX_2 adducts were readily formed. The adducts of ruthenocene and osmocene with HgX_2 have donor—acceptor M—Hg bonding [21] which has been observed with other transition metal π-complexes [39—43]. In the formation of such bonding the π-complexes behave as donors with an electron pair in a non-bonding orbital, generally metallic. The Lewis basicity of the metal in metallocenes could be estimated quantitatively by comparison of the total stability constants of generated adducts. A comparison of k_2 values determined in the present work for ruthenocene ($10^{11\,2}$) and osmocene ($10^{19\,5}$ mol^{-1}) shows that Lewis basicity of Os is higher than that of Ru. Similar enhancement of the donor properties upon downward comparison in Groups in the Periodic Table has been reported for Rh and Ir and also for other Ru and Os complexes [44].

On the basis of these ideas one may suggest that unlike ferrocene which releases an electron (but not the pair of electrons) upon oxidation and adduct formation with acceptors, ruthenocene and osmocene are oxidized with loss of two electrons, and they prefer compounds which accept an electron pair for bond formation.

Experimental

Polarographic measurements

The polarograms were registered on OH-102 polarographs and using a TsLA model 02A oscillopolarograph with a device providing triangular voltage. The measurements were performed using a trielectrode scheme. The working electrodes were a DME (m = 2.5 mg/sec, t = 0.15 sec) and a rotating disc Pt electrode (rotational speed 650 min^{-1}, s = 0.8 mm^2) and a Pt net was the auxiliary electrode. The reference electrode ($Ag/AgClO_4$ 0.01 N in 0.1 N Et_4NClO_4 in CH_3CN) was connected with working solution by a bridge whose end was closely located at the working electrode. Its potential (with respect to SCE) was + 0.343V. The volume of polarographic solution was 10 ml. The dissolved oxygen was removed by bubbling argon through the solution.

Preparations

The solvent CH_3CN and phone electrolytes Bu_4NBF_4 and EtNBF were purified by methods described in refs.45 and 46 respectively. $[(C_5H_5)_2Ru]_2Hg(BF_4)_2$ was prepared as in ref.16.

Electrolysis at the controlled potential

The working potential was maintained with P-5827 potentiostat at an accuracy of ± 0.003V. The electrolysis was carried out in a cylindrical cell with diaphragm (porous filter no.3 and ceramics). The volume of solution in the space of working (Hg, Pt) and auxiliary electrodes (Pt net) was 50—60 and 5—10 ml respectively. The electrode of comparison was $Ag/AgClO_4$, 0.01 N in 0.1 N Et_4NClO_4 solution in CH_3CN. In all cases CH_3CN was used as solvent and 0.1 N Et_4NBF_4 or Bu_4NBF_4 served as phone electrolytes. The amount of electricity passed during the electrolysis was determined by means of a digital current intgrator. Basic parameters of the electrolysis of the compounds investigated are listed in Table 2.

TABLE 2

BASIC PARAMETERS OF THE ELECTROLYSIS OF FERROCENE, RUTHENOCENE AND OSMOCENE AT CONTROLLED POTENTIAL (CH_3CN, 0.1 *N* Et_4NBF_4)

Compound	Working electrode	Potent. of elect.[a]	Reacted subs. (g)	Initial current (mA)	Current at the end of electrolysis (mA)	Electrolysis time (min)	Amount of electricity		Number of electrons
							Exp. (g)	Calcd. (g)	
$(C_5H_5)_2Fe$	Hg	0.20	0.0354	32	0.65	35	17	18.4	1
	Pt	0.20	0.0423	25	2.5	20	18.2	22.0	1
$(C_5H_5)_2Ru$	Hg	0.15	0.066	40	5.5	60	35	30	1
	Pt	0.85	0.1391	80	0.2	120	118	116.2	2
$(C_5H_5)_2Os$	Hg	0.30[b]		150	5	15			1
	Pt	0.80	0.1440	50	1.3	200	43	43.4	1

[a] With respect to $Ag/AgClO_4$; 0.01 *N* in CH_3CN, 0.1 *N* Et_4NClO_4. [b] With respect to SCE.

The electrolysis of ferrocene. To remove the impurities the phone electrolyte was electrolyzed at $E = +0.20V$ for 20—25 min. On electrolysis on the rotating mercury anode the polarogram of the electrolyzed solution manifests the absence of mercury ions which might have been present because the electrolusis potential was close to that of anodic dissolution of mercury. After addition of ferrocene a change of colour from orange to green and then blue was observed in the course of electrolysis. After electrolysis the UV spectrum of the solution had the band at $\lambda_{max} = 616$ nm, $\log\epsilon = 2.3$ (lit. [47] $\lambda_{max} = 617$, $\log\epsilon = 2.53$) specific of the ferricinium cation.

The electrolysis of ruthenocene and osmocene on the rotating mercury anode. The phone electrolyte solution was preliminary electrolyzed at + 0.15V in the case of ruthenocene and 0.15V (with respect to SCE) for osmocene. The polarogram of solution after electrolysis showed that no mercury ions transfer into the solution at such potentials. After addition of a metallocene sample the solution rapidly became yellow. After the electrolysis the solvent was evaporated and phone electrolyte was removed by washing with alcohol (because of its good solubility*). The UV. IR and polarograms of the yellow residue were identical to those of $[(C_5H_5)_2M]_2Hg(BF_4)_2$ chemically prepared.

The electrolysis of ruthenocene on the Pt electrode. The solution of phone electrolyte and ruthenocene was electrolyzed at $E = +0.85V$ for 30 min. The solution had a brown colour after electrolysis. After the electrolysis the solvent was evaporated and the residue extracted with benzene to remove unreacted ruthenocene. Phone electrolyte was washed out with cold alcohol. After evaporation of the alcohol the residue was analyzed by polarography and IR spectra. The polarogram (DME or Pt electrode, CH_3CN, 0.1 *N* Et_4NBF_4) had no cathodic wave which could be assigned to $(C_5H_5)Ru^{2+}$ reduction (in the region of higher positive potentials than $E_{1/2}$ $[(C_5H_5)_2RuCl]^+ = -0.03V$ (Table 1), and the IR spectrum showed no band specific of the π-bonded C_5H_5 ring. The reduction of acidified aqueous reaction mixture with $SnCl_2$ yielded no ruthenocene.

The electrolysis of osmocene on the Pt electrode. The electrolysis of solution of phone electrolyte and osmocene was carried out at + 0.80V. The elec-

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* At the electrolysis of $(C_5H_5)_2Ru$ the residue was washed with ether to remove the traces of unreacted ruthenocene.

orlysis of $(C_5H_5)_2Os$ on the Pt electrode resulted in precipitation of a dark green solid which was removed in the course of formation. The solution gradually turned light brown. The polarogram and UV spectrum of the electrolyzed solution confirm the absence of unreacted $(C_5H_5)_2Os$. The dark green substance $[(C_5H_5)_2OsBF_4]$ from the electrode and solution was washed with alcohol and ether. (Anal. found: C, 29.19, 29.07; H, 2.57, 2.74. $(C_5H_5)_2OsBF_4$ calcd.: C, 29.49; H, 2.47%.) Yield 54% based on $(C_5H_5)_2Os$. The substance is insoluble in CH_3CN, DMF, pyridine, alcohol and ether, soluble in water (green solutions). The aqueous acidified solution became colourless upon reduction with acidic (HCl) solution of $SnCl_2$. The reaction mixture was extracted with benzene. The benzene extract was chromatographed (on alumina in petroleum ether) and polarographed (on the Pt electrode in CH_3CN, 0.1 *N* Et_4NBF_4) to reveal osmocene. The IR spectrum of the solid salt had a band at 3100 cm^{-1} which could be assigned to C—H modes in the C_5H_5 ring. The BF_4^- vibrational frequencies at 550—1500 cm^{-1} are superimposed on those of $(C_5H_5)_2Os^+$ and hinder their assignment.

Oxidation of ruthenocene with ferric chloride. The oxidation procedure was similar to that described for ferrocene [48,49]. 0.3 g of ruthenocene in 30 ml of absolute ether and 1.27 g of anhydrous $FeCl_3$ in 50 ml of absolute ether gave 0.3 g of $C_{10}H_{10}RuFeCl_5$ crystallized from glacial acetic acid. (Anal. found: C, 25.95, 26.09; H, 2.19, 2.20; Cl, 38.10. $C_{10}H_{10}Cl_5FeRu$ calcd.: C, 25.86; H, 2.17; Cl, 38.17%.)

The reaction of ruthenocene with bromine. A solution of 0.096 g of Br_2 (0.0006 mol) in 10 ml of absolute CCl_4 was gradually added to 0.15 g of ruthenocene (0.0006 mol) in 12 ml of absolute CCl_4. The green solid precipitated in the course of bromine addition was filtered off washed with CCl_4, petroleum ether and dried. 0.22 g of $C_{10}H_{10}RuBr_5$ was obtained. (Anal. found: C, 21.79, 21.90; H, 1.97, 1.83. $C_{10}H_{10}Br_5Ru$ calcd.: C, 21.80; H, 1.83%.)

The synthesis of $[(C_5H_5)_2Os]_2Hg(BF_4)_2$. The procedure was similar to the synthesis of $[C_5H_5)_2Ru]_2Hg(BF_4)_2$ [16]. 5 drops of ca. 40% HBF_4 were added to a solution of 0.1 g (0.34 mmol) of $(C_5H_5)_2Os$ and 0.04 g (0.16 mmol) of $Hg(CN)_2$ in absolute C_2H_5OH. The yellow solid precipitated (0.13 g) was filtered off and washed with alcohol. The compound was identified by UV and IR spectra. The UV spectrum of compound in 0.01 *N* $HClO_4$ solution had the band at λ_{max} = 300 mn, log ϵ = 4.3.

Complexes of metallocenes with HgX_2 $(X = Cl, Br)$

Ferrocene complex with $HgCl_2$. 2.1 g (0.011 mol) of ferrocene triturated with 1 g (3.7 mmol) of $HgCl_2$ in the presence of 1 ml of absolute ethanol. The red complex generated was washed with benzene and petroleum ether on the filter to remove unreacted ferrocene. 1.5 g (22%) of $C_{10}H_{10}Fe \cdot 6HgCl_2$ was obtained. (Anal. found: C, 6.21, 6.30; H, 0.46, 0.44; Cl, 23.60, 23.70; Fe, 3.11, 3.42; Hg, 65.42, 65.40. $C_{10}H_{10}Cl_2FeHg$ calcd.: C, 6.61; H, 0.56; Cl, 23.46; Fe, 3.08; Hg, 66.28%.)

Ruthenocene complex with $HgCl_2$. A solution of 0.54 g (2 mmol) of $HgCl_2$ in 15 ml of alcohol was added to 0.5 g (2 mmol) of ruthenocene in the mixture of 80 ml of alcohol and 20 ml of benzene. The lemon yellow solid immediately precipitated was filtered off washed with benzene and alcohol. 0.71 g (65%) of the complex was obtained, m.p. (dec.) > 200° (from CH_3CN). (Anal.found: C, 23.85, 24.02; H, 2.00, 2.05; Cl, 14.08, 14.07. $C_{10}H_{10}Cl_2HgRu$ calcd.: C, 23.89; H, 2.00; Cl, 14.12%.

Osmocene complex with $HgCl_2$. Analogously to the ruthenocene complex with $HgCl_2$ this was obtained from 0.3 g (0.93 mmol) of osmocene and 0.25 g (0.93 mmol) of $HgCl_2$. Yield 0.51 g (90.2%). M.p. (dec.) > 250° (from CH_3CN). (Anal. found: C, 20.27, 20.45; H, 1.92, 1.74; Cl, 11.88, 11.55; Hg, 33.38, 33.91 Os, 31.96, 32.30. $C_{10}H_{10}OsHgCl_2$ calcd.: C, 20.29; H, 1.70; Cl, 11.89; Hg, 33.89; Os, 32.13%.)

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