Complexes of rhodium carbonylchloride and phosphorus(III) cyanides in mediated electrochemical reduction of 2-carbomethoxy-2-methyl-1,1-dichlorocyclopropane

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Electrochemical reduction of the complexes $Rh(CO)ClL_2$ [L = $(EtO)_2PCN$ (**1**), Ph_2PCN (**2**)] and $Rh_2(CO)_4L$ [L = $P(CN)_3$ (**3**),  $PhP(CN){-}P(CN)Ph$ (**4**)] and their catalytic properties in electrochemical reduction of 2-carbomethoxy-2-methyl-1,1-dichlorocyclopropane were studied. The catalytic electroreduction of a substrate at the reduction potentials of the central ion was developed for complexes **2**—**4**. This process is accelerated substantially for complexes **2** and **3** in the presence of anthracene.

Key words: electrochemistry, metal complexes, dichlorocyclopropane, kinetics, reduction.

Previously we have found[1—3] the phenomenon of homogeneous reduction of organobromine and -chlorine compounds by electrochemically generated radical anions of organic compounds catalyzed by Pt^{II}, Pd^{II}, Rh^{III}, Ni^{II}, and Co^{II} ions and aminomethylphosphine complexes of Pt^{II}, Pd^{II}, and Ni^{II}.

$$A + e \rightleftharpoons A^{\cdot -}$$

$$A^{\cdot -} + B{-}X \longrightarrow A + X^- + \text{products} \quad (k_{\text{eff}}{}^{A})$$

$$A^{\cdot -} + M^{n+} + B{-}X \longrightarrow$$

$$\longrightarrow A + M^{n+} + X^- + \text{products} \quad (k_{\text{eff}}{}^{A,MC})$$

$$k_{\text{eff}}{}^{A,M} \gg k_{\text{eff}}{}^{A}.$$

To continue studying processes involving double mediated systems, the kinetics of electrochemical reduction of 2-carbomethoxy-2-methyl-1,1-dichlorocyclopropane (BX) involving anthracene (A) and complexes of rhodium carbonylchloride and phosphorus(III) cyanides were studied in this work.

Experimental

The kinetics of homogeneous reduction were studied by polarography in DMF against 0.1 M Bu_4NBF_4. The procedures for purifying solvents and supporting salts, polarographic measurements, and calculation of kinetic parameters were described previously.[2] Parameters of the capillary: m_{Hg} = 0.71 mg s^{-1}, t = 0.5 s. The frequency of reversing potentials was 10 Hz. Bottom mercury with a potential of −0.14 V relative to an SCE was used as the reference electrode. Procedures of synthesis, purification, and identification of complexes are similar to those presented previously.[4]

Results and Discussion

Electrochemical parameters of reduction waves of the metal complexes studied and the corresponding ligands are presented in Table 1. At the first stage, all complexes are reduced at low cathodic potentials. A substantial effect of the nature of the phosphine ligand on $E_{1/2}$ of the complex is observed in the series of compounds **1**—**4**. The introduction of electron-withdrawing nitrile groups considerably facilitates the reduction of both the ligand and the complex. However, in the general case there is no direct correlation between the $E_{1/2}$ values of reduction of the complex and the ligand. For example, $(EtO)_2PCN$ is reduced with more difficulty than Ph_2PCN, while the corresponding complex **2** is reduced easier than complex **1**.

Reduction of phosphine metal complexes is accompanied, as a rule, by electron transfer primarily to central ion.[5] The reduction of the complexes studied at the first-wave potentials is likely also to change the oxidation degree of the central ion that is indicated by the great difference in reduction potentials of the complex and the ligand. Reduction products are unstable that is

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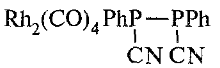
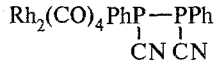
Table 1. Electrochemical parameters of reduction waves for complexes **1—4** and ligands

Complex		$-E_{1/2}$/mV	$\frac{E}{\lg[i / (i_{\lim} - i)]}$ /mV	i_a/i_c
$Rh(CO)Cl[(EtO)_2PCN]_2$	**(1)**	0.5	50	0.47
		1.38	150	*
$Rh(CO)Cl[Ph_2PCN]_2$	**(2)**	0.68	80	0.38
		1.71	470	*
$Rh_2(CO)_4P(CN)_3$	**(3)**	0.43	100	0.55
		1.4	370	*
		2.13	160	*
 $Rh_2(CO)_4\underset{CN}{PhP}-\underset{CN}{PPh}$	**(4)**	0.73	180	*
Ph_3P	**(5)**	2.08	63	0.7
Ph_2PCN	**(6)**	1.92	80	*
		2.08	70	*
		2.59	50	*
$P(CN)_3$	**(7)**	1.66	170	*
$(EtO)_2PCN$	**(8)**	2.14	100	*
		2.50	90	*

Note. Conditions: DMF, 0.1 *M* Et_4NBF_4 as a background, 25 °C. * Irreversibly.

Table 2. Effective rate constants of catalytic electroreduction of 2-carbomethoxy-2-methyl-1,1-dichlorocyclopropane in the presence of rhodium complexes

Complex		k_{eff}		
		MC	MC,A	A,MC
$Rh(CO)Cl[(EtO)_2PCN]_2$	**(1)**	No increase		2000
$Rh(CO)Cl[Ph_2PCN]_2$	**(2)**	35	280	700
$Rh_2(CO)_4P(CN)_3$	**(3)**	750	2200	1200
 $Rh_2(CO)_4\underset{CN}{PhP}-\underset{CN}{PPh}$	**(4)**	1300	420	2300

Note. Conditions: DMF, 0.1 *M* Et_4NBF_4 as a background, 25 °C, C_{MC} = $2 \cdot 10^{-4}$ mol L^{-1}, C_A = $1 \cdot 10^{-3}$ mol L^{-1}, C_{VC} = $1 \cdot 10^{-2}$ mol L^{-1}. In the absence of the complex $k_{eff}{}^{A}$ = 670 m^{-1} s^{-1}.

evidenced by the absence of anodic commutated current in the case of complex **4** and low values of i_a/i_c for other complexes (see Table 1). In a series of related compounds **1—4**, according to the Mairanovskii rule of antiparallelism (see Ref. 6), a reduction product is less stable for complexes that are reduced more difficult.

When substrate BX is added to a solution of complex **1**, the polarogram corresponds to the additive curve of the individual complex and the substrate. In the case of other complexes, there is an increase in the limiting value of the reduction wave of the complex to indicate the catalytic reduction of the substrate. Effective rate constants of homogeneous reduction of the substrate by the metal complex ($k_{eff}{}^{MC}$) were calculated from the catalytic increase of the current. The same constants in the presence of anthracene ($k_{eff}{}^{MC,A}$) and for the reduction of the substrate by anthracene radical anions in the presence of the metal complex ($k_{eff}{}^{A,MC}$) are presented in Table 2. The catalytic activity of the complexes and their redox properties depend on the ligand surroundings. Among the complexes studied, complex **3** is the most active and complex **1** is the least active. The rate of catalytic reduction of the substrate at the potentials of the first reduction wave of complexes **2** and **3** increases substantially in the presence of anthracene (see Table 2).

The concentration of complex **3** is equal to $2 \cdot 10^{-4}$ mol L^{-1}, which corresponds almost to its limiting solubility in DMF. No similar effects were observed for double mediated reduction of the systems anthracene—metal ions and anthracene—aminomethylphosphine complexes of organobromine and -chlorine compounds. The superposition of catalytic effects of mediators of two types was observed only at reduction potentials of anthracene. A similar effect is also observed in the systems studied in the case of complexes **2** and **4**, and an insignificant increase in $k_{eff}{}^{A,MC}$ compared to $k_{eff}{}^{A}$ is likely to be caused by low concentrations of metal complexes.

The contribution of anthracene to homogeneous reduction of the substrate at reduction potentials of the complex is the distinguishing feature of the double mediated systems used in this work. Anthracene is reduced at considerably more negative potentials, and, hence, its catalytic effect is caused by the participation of anthracene molecules rather than its radical anions in the process. It is likely that the products of the reduction of metal complexes form other complexes with anthracene that are more active toward the substrate.

References

1. V. V. Yanilkin, N. I. Maksimyuk, E. I. Strunskaya, B. M. Garifullin, and Yu. M. Kargin, *Izv. Akad. Nauk, Ser. Khim.*, 1993, 1407 [*Russ. Chem. Bull.*, 1993, **42**, 1340 (Engl. Transl.)].
2. V. V. Yanilkin, N. I. Maksimyuk, E. I. Strunskaya, A. A. Karasik, and Yu. M. Kargin, *Izv. Akad. Nauk, Ser. Khim.*, 1994, 414 [*Russ. Chem. Bull.*, 1994, **43**, 372 (Engl. Transl.)].
3. V. V. Yanilkin, N. I. Maksimyuk, and Yu. M. Kargin, *Izv. Akad. Nauk, Ser. Khim.*, 1994, 1022 [*Russ. Chem. Bull.*, 1994, **43**, 957 (Engl. Transl.)].
4. V. N. Nazmutdinova, L. P. Chirkova, R. M. Mukhamadieva, A. Kh. Plyamovatyi, R. M. Gainullin, M. A. Pudovik, V. K. Polovnyak, and A. N. Pudovik, *Zh. Obshch. Khim.*, 1994, **64**, 1617 [*J. Gen. Chem.*, 1994, **64** (Engl. Transl.)].
5. G. K. Budnikov, *Elektrokhimicheskie reaktsii khelatov metallov v organicheskikh i smeshannykh rastvoritelyakh* [*Electrochemical Reactions of Metal Chelates in Organic and Mixed Solvents*], Kazan' Univ., Kazan', 1980, 176 (in Russian).
6. V. G. Mairanovskii, *Dokl. Akad. Nauk SSSR*, 1985, **284**, 386 [*Dokl. Chem.*, 1985, **284** (Engl. Transl.)].

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