Electrocatalytic reduction of organic halides with cobalt bipyridine complexes

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The electrocatalytic reduction of organic halides by the $[Cobpy]^+$ complexes coordinationally unsaturated with bpy (at potentials of the first wave) and by the coordinationally saturated $[Cobpy_2]^-$ complexes (at potentials of the second wave) was observed. The apparent rate constant of the process decreased with an increase in the difference of the reduction potentials of the substrate and catalyst in a large range of the driving force of the process.

Key words: cobalt complexes, 2,2'-bipyridine, organic halides, homogeneous electrochemical catalysis.

 σ -Complexes of transition metals with organic ligands can often be key intermediates of electrocatalytic processes. Data on their nature and electrochemical and chemical processes are necessary for the simulating of particular stages and elucidation of the reaction mechanism. Such a diagnostics using electrochemical methods provides preliminary conclusions on the reaction mechanism without isolation of intermediates from the appearance of new reduction or oxidation waves.

Using the Ni⁰ and [Ni⁰L]^{•-} nickel complexes, we have previously shown¹ that the Ni⁰ complex acts as the inner-sphere electron mediator reducing organic halides (RX) to form the RNiX σ -complexes, and the radical anion [Ni⁰L]^{•-} complexes exhibit intermediate properties characteristic of Ni⁰ and L^{•-} (outer-sphere mediator). In this work we studied the electrochemical reduction (ER) of the Co^{II} complexes with 2,2′-bipyridine (bpy) in MeCN and DMF solutions with different numbers of ligands in the presence of RX (R = Alk, Ar, Het). The study also included determination of the reactive form of the complexes, estimation of the reactive swith the data obtained previously for the nickel complexes.^{2–6}

Experimental

The products of preparative electrolysis at the controlled current or potential were analyzed by ¹H NMR spectroscopy, GLC, and elemental analysis. ¹H NMR spectra were recorded on a Varian T-60 instrument (60 MHz) relatively to the internal standard Me₄Si. GLC analysis was carried out on a Chrom chromatograph (flame-ionization detector, helium as carrier gas, glass column (120 cm \times 3 mm, 5% Silicon OV-17 on Chromaton N-AW-DMCS, 0.16–0.20 mm)).

The electroreduction of the cobalt complexes in the absence and presence of the starting substrates and organyl halides was studied by cyclic voltammetry (CV). Cyclic voltammograms were recorded on platinum (1.5 mm in diameter) or gold (1.0 mm in diameter) electrodes. A silver electrode Ag/AgNO₃ served as the reference electrode, and 0.01 M solutions of AgNO₃ in MeCN were used. A platinum wire 1 mm in diameter and 10 mm in length was used as the auxiliary electrode. Measurements were carried out in a cell with the temperature maintained at 25 °C in an argon atmosphere. Voltammograms were recorded on a PI-50-1 potentiostat with a PR-8 programmer and an electrochemical cell, which was connected by the threeelectrode scheme. The curves were recorded at a linear potential scan rate of 50 mV s⁻¹ on a two-coordinate recorder. In experiments on ER, a substrate was added to a solution of the cobalt complex $(1 \cdot 10^{-2} \text{ mol } \text{L}^{-1})$ using a 10-µL syringe.

Preparative electrolysis was carried out using a B5-49 d.c. power source in a 4-mL three-electrode cell with a constant temperature in DMF. The potential of the working electrode was measured using a Shch-1312 d.c. voltmeter relatively to the reference electrode Ag/0.01 M AgNO₃ in the corresponding solvent. In experiments on undivided electrolysis a magnesium rod was used, whose working surface was thoroughly cleaned with an emery paper before electrolysis.

In experiments with divided electrolysis a paper was used as the diaphragm, a glass-carbon plate with a working surface area of 4 cm² served as the anode, and the anolyte was a saturated solution of the background, which was used in the catholyte, in the corresponding solvent. In all cases, a nickel network with a geometric surface area of 15 cm² was the cathode. During electrolysis the electrolyte was stirred with a magnetic stirrer at a constant argon flow.

To prepare the CobpyBr₂ complex, CoBr₂·6H₂O ($5 \cdot 10^{-2}$ mol) was dissolved in EtOH (100 mL), the mixture was stirred for 3 h until the salt dissolved completely, and 2,2'-bipyridine ($5 \cdot 10^{-2}$ mol) was added with continuous stirring. After 10–12 h the precipitated residue of CoBr₂bpy was filtered off and dried for 1 day in a vacuum desiccator at 30 °C.

Published in Russian in *Izvestiya Akademii Nauk. Seriya Khimicheskaya*, No. 9, pp. 1562–1568, September, 2002. 1066-5285/02/5109-1702 \$27.00 © 2002 Plenum Publishing Corporation The $[Co(bpy)_3](BF_4)_2$ complex was synthesized similarly, namely, $Co(BF_4)_2 \cdot 6H_2O$ (5 · 10⁻² mol) was dissolved in EtOH until the crystals dissolved completely, 2,2'-bipyridine (1.5 · 10⁻¹ mol) was added, and the mixture was stirred for 8–10 h. The precipitate of Co(bpy)_3(BF_4)_2 that formed was filtered off and dried in a vacuum desiccator analogously to CobpyBr₂.

Tetraalkylammonium tetrafluoroborates were used as supporting salts. The Et_4NBF_4 salt was prepared by the neutralization of HBF₄ with tetraethylammonium hydroxide, triply recrystallized from aqueous EtOH, and dried *in vacuo* for 72 h at 30 °C. The solvent (MeCN) was purified by triple distillation above P_2O_5 and KMnO₄, and the middle fractions were used for voltammetry. Commercial DMF was distilled *in vacuo*, dried for 3 days above molecular sieves 4A, pre-calcined in a vacuum furnace at 100 °C, and dried for 1 day above anhydrous K₂O₃. Then the solvent was decanted and twice fractionally distilled *in vacuo*.

Commercial reagents (reagent grade) used as references in GLC were purified by either distillation (liquid) or recrystallization from hexane to their unvariable physical constants.

The preparative reduction of CobpyBr₂ $(1.7 \cdot 10^{-2} \text{ mol } \text{L}^{-1})$ in the presence of MesBr (Mes is mesityl) $(3.4 \cdot 10^{-2} \text{ mol } \text{L}^{-1})$ was carried out at -1.3 V in a divided cell using a solution of Et₄NBr in DMF as supporting electrolyte. After 1.2 *F* electricity per CobpyBr₂ were passed, the MesCoBrbpy complex (0.16 g, 84%) was isolated from the reaction mixture. Found (%): C, 56.0; H, 6.02; N, 5.12; Co, 13.03; Br, 19.83. Calculated (%): C, 55.1; H, 4.59; N, 6.76; Co, 14.25; Br, 19.32. ¹H NMR (CDCl₃), δ : 8.56–8.57 (m, 2 H); 8.33–8.37 (d, 2 H); 7.79–7.82 (m, 2 H); 7.28–7.31 (m, 2 H); 6.45 (m, 2 H, C₆H₂); 2.59 (s, 6 H, Me); 2.17 (s, 3 H, Me).

Results and Discussion

Cyclic voltammetry of 2,2[']-bipyridinecobalt(II) complexes. The reduction of the $\text{Co}^{2+}\text{bpy}_n$ (n = 1-3) complex cations at the Pt electrode in MeCN (Table 1) is characterized by two diffusion-controlled peaks in the voltammetric curve. This is confirmed by linear dependence of the current on the square root of the potential

Table 1. Parameters of the peaks of electrochemical reduction of the Co^{II} complexes with 2,2'-bipyridine in MeCN at the Pt electrode

Complex	$-E_{\rm p}^{-1}$ /V	<i>i</i> _p ¹ /μΑ	$(i_{\rm a}/i_{\rm c})^1$	$-E_{\rm p}^{2}$ /V	<i>i</i> _p ² /μΑ	$(i_{\rm a}/i_{\rm c})^2$
Cobpy(BF ₄) ₂	1.33	25	0.3	1.89	28	0.35
$Cobpy_2(BF_4)_2$	1.30	30	0.8	1.89	65	0.48
$Cobpy_3(BF_4)_2$	1.24	30	0.9	1.89	65	0.70

Note. The following designations were used: E_p^{1} and E_p^{2} are the potentials and i_p^{1} and i_p^{2} are the currents of the first and second peaks of reduction of complexes, respectively; i_a/i_c is the ratio of the anodic and cathodic peaks of currents for the forward and reverse potential scans.



Fig. 1. Cyclic voltammogram for $Co^{II}bpy_3$ (1 · 10⁻² mol L⁻¹) at the Pt electrode in a solution of Et₄NBF₄ in MeCN.

scan rate. It is seen from the data in Table 1 that the $Co^{I}bpy_{n}$ complex forms at potentials of the first, oneelectron peak (E_p^{-1}) , while at potentials of the second peak $(E_{\rm p}^2)$ the number of transferred electrons is 1e for n = 1 and 2e for n = 2-3. Thus, the electrochemical behavior of the cobalt complexes with 2,2'-bipyridine depends on the number of ligands bound to the metal. It can be assumed that the unstable 17-electron $Co^0 bpy_n$ complex (n = 1, 2) for n = 1 or 18-electron Cobpy_n⁻ complex for n = 2, 3 is formed at E_p^2 (Fig. 1). No paramagnetic cobalt species were found in the products of electrochemical reduction of the [Cobpy₃](BF₄)₂ complexes in the accessible potential region studied by ESR (although it should be admitted that cobalt species are complicated objects for ESR studies), *i.e.*, unlike similar nickel complexes for which paramagnetic $Ni(0)[L^{-}]$ is formed at the second wave,¹ Cobpy_n⁻ is rather an anionic complex.

Thus, bpy forms complexes with cobalt in different oxidation states, and the presence of pairs of redox peaks in the CV curves (see Fig. 1) point to the relative stability of these complexes. These facts indicate that the Co—bpy system can be used in homogeneous electrocatalysis, for example, for the dehalogenation of organic substrates.

It can be expected that $Co^{l}bpy_{n}$ (formed at potentials of the first peak) or $Cobpy_{n}^{-}$ assumed by us (formed at potentials of the second peak) are the catalytically active forms of the cobalt compounds with bpy. The reactivity of these complexes can depend on the number of ligands bound to the metal.

Catalysis by the cobalt complex coordinationally saturated with bpy. Let us consider the electrochemical behavior of the $[Co^{2+}bpy_3](BF_4)_2$ complex in the presence of RX. When RX (chloro-, bromo-, and iodobenzene, 1-bromo-2-methylbenzene, 2-chlorothiophene, 2-bromopyridine, 1-iodohexane, 1-iodo-1-methylethane, and 1-iodo-3-methylbutane) is added to a solution of the cobalt complexes, an increase in the current of the cathodic peaks is observed in the voltammetric curves. This effect can serve as a quantitative characteristic of the catalytic properties of the complex. It was found that under experimental conditions the Co^I complex did not manifest catalytic properties (the reversibility of the Co^{II}/Co^I wave remained unchanged and the catalytic effect was absent) toward all substrates except allyl bromide. However, the height of the second peak corresponding, as we believe, to the reduction of Co^I to [Cobpy₂]⁻ increases when the substrate is added, and the anodic peak disappears at the reverse scan (*i.e.*, the electrochemical "reversibility" disappears). Thus, in this case, the complex anion, whose regeneration during electrolysis provides an increase in the current, is catalytically active (Scheme 1).

Scheme 1

$$Co^{1}bpy_{2} + 2 e \implies [Cobpy_{2}]^{-} = Co^{-}bpy_{2}$$

$$Co^{-}bpy_{2} + RX \implies [R-Co^{1}]bpy_{2} + X^{-}$$

$$[R-Co^{1}]bpy_{2} \implies [R^{-}] + Co^{1}bpy_{2}$$

The scheme proposed explains, as a whole, the effects observed: the increase in the current of the second cathodic peak and the total irreversibility of the process due to the fast subsequent chemical reaction. The latter results in the formation of a species, which is the donor of the R[•] radical or contains a weakly bound radical capable of further transferring from one reactant to another. The generated R' species can be dimerized, reduced to R⁻, enter into other reactions of the radical or anionic type. The dependence observed in several cases for k_{app}^{I} on the substrate concentration⁷ indicates the first order of the reaction (Fig. 2). All plots like those presented in Fig. 2 are linear and pass through the origin of coordinates because $k_{app}^{I} = k_{app}^{II} C_{RX}$. However, the error in calculation of k_{app}^{I} in the region of low C_{RX} is rather high and, therefore, the straight line can bend near the coordinate origin. Using the data in Fig. 2, we can find the k_{app}^{II} rate constant and determine the series of reactivity toward [Cobpy₂]⁻ for various substrates: 2-chlorothiophene < PhBr < 2-bromopyridine < 2-bromotoluene < PhCH₂Cl < PrⁱI < C₆H₁₄I < PhI.

The catalytic effect was found at potentials of the assumed reduction $\text{Co}^+\text{bpy}_2 \rightarrow [\text{Cobpy}_2]^-$ for the following substrates: Pr^iI , 2-bromotoluene, *n*-hexyl iodide, 2-bromopyridine, 2-chlorothiophene, PhCH₂Cl, PhBr, and PhI. In the case of bromomesitylene, PhCl, and BuCl, catalysis is absent, probably, due to the slower cleavage of the C—Hal bonds or steric hindrance of the



Fig. 2. Plot for the apparent rate constant (k_{app}^{I}) of regeneration of the $[Co(bpy)_2]^-$ (1-8) and $[Cobpy_n]^+$ (9) catalysts *vs.* RX concentration: RX is 2-chlorothiophene (1), PhBr (2), 2-bromopyridine (3), 2-bromotoluene (4), PhCH₂Cl (5), Pr^II (6), C₆H₁₃I (7), PhI (8), and AllBr (9).

reaction center (bromomesitylene), which decreases the rate constants of the oxidative addition and reductive elimination.

It is of interest that in the presence of allyl bromide catalytic regeneration is observed already at potentials of the first peak of $\text{Co}^{2+}\text{bpy}_3$ reduction, *i.e.*, the reduction of RX by Co^+bpy_2 occurs rather rapidly (see Fig. 2). This process is also characterized by a linear dependence of k^{I}_{app} on the substrate concentration.

Thus, the CV data prove the catalytic increase in the current of reduction of the mediator complexes when the RX substrates are added and allow the estimation of the potential of regeneration of the cobalt complex in the catalytic cycle. Based on the current characteristics of the process, we attempted to estimate the rate constant of the catalytic reaction. In the case of the [Cobpy₃]²⁺ complex coordinationally saturated with bpy, the catalytic effect and the gain in the corresponding current are observed only at potentials of the second reduction wave corresponding to the formation of the intermediate [Cobpy₂]⁻ complex (except the case of allyl bromide), and the apparent rate constant of catalyst regeneration k^{II}_{app} for the RX studied is 30–160 mol⁻¹ L⁻¹ s⁻¹ (Table 2).

Table 2. Potentials of the reduction peaks (E_p) of organic halides (RX) on the Pt electrode and rate constants of catalyst regeneration k^{II}_{app} in the presence of the Co^{II}bpy₃ and Co^{II}bpy catalyst precursors

RX ^a	$-E_{\rm p}/{\rm V}$	$k^{\rm II}_{\rm app} \cdot 10^{-2} / \rm{mol}^{-1} \ \rm{L}^{-1} \ \rm{s}^{-1}$		
		Co ^{II} bpy ₃ ^b	Co ^{II} bpy ^c	
PhBr	2.82	0.2	_	
PhI	_	0.5	_	
2-Chlorothiophene	_	2.56	0.2	
2-Bromopyridine	2.30	2.35	_	
2-MeC ₆ H ₅ Br	2.23	0.6	0.1	
PhCH ₂ Cl	2.11	1.0	_	
Me ₂ CH(CH ₂) ₂ I	2.09	0.7	0.3	
Me ₂ CHI	2.07	1.0	_	
$C_6 H_{13}I$	1.97	0.9	0.4	
CH ₂ =CH–CH ₂ Br	1.97	0.9	1.0	

^{*a*} The concentration of RX was $1.5 \cdot 10^{-1}$ mol L⁻¹.

^b The concentration was $5 \cdot 10^{-3}$ mol L⁻¹, $E_p^2 = -1.89$ V. ^c The concentration was $5 \cdot 10^{-3}$ mol L⁻¹, $E_p^2 = -1.31$ V.

The $\log k^{II}_{app}$ values decrease with an increase in the difference of the reduction potentials of the complex (A) and substrate (RX) $\Delta E_p^{A-RX} = E_p^A - E_p^{RX}$ (Fig. 3).

The reaction is likely inner-sphere, and reductive elimination is the probable limiting stage, as it was found for the nickel complexes with bpy.⁸ For processes involving iodobenzene, 1-iodohexane, 1-bromo-2-methylbenzene, and 2-chlorothiophene we determined k_{app}^{II} for the reduction of one substrate by various complexes. The slopes of the lines connecting the points for one RX and different complexes $(\Delta \log k^{II}_{app}/\Delta \Delta E_p^{A-RX})$ are $1/1200 \text{ mV}^{-1}$ on the average, which is by an order of magnitude lower than the value characteristic of classical outer-sphere activation processes of intermolecular electron transfer $(1/120 \text{ mV}^{-1})$.⁹

Catalysis by the complex coordinationally unsaturated *with bpy*. The reduced forms of the [Cobpy]⁺ complex



Fig. 3. Plot of $\log k^{II}_{app}$ for reduction of organic halides RX by the $[Cobpy]^+$ and $[Cobpy_2]^-$ cobalt complexes vs. difference of reduction potentials of the complexes (A) and substrates (RX) ΔE_{p}^{A-RX} : A = Co^{II}bpy₃ (E_{p}^{2} -1.89 V) (1–4), Co^{II}bpy (E_{p}^{1} -1.31 V) (1'–4'); RX = C₆H₁₃I (1, 1'), Me₂CH(CH₂)₂I (2, 2'), 2-MeC₆H₅Br (3, 3'), and 2-chlorothiophene (4, 4').

coordinationally unsaturated with bpy exhibit a higher catalytic activity in the reduction of organic halides. For example, the catalytic gain in the current is observed already at potentials of the first peak of reduction $[Cobpy]^{2+} + e^- \rightarrow [Cobpy]^+$ in the presence of iodobenzene, 1-bromo-2-methylbenzene, 2-chlorothiophene, 1-iodohexane, and 1-iodo-3-methylbutane. The current gains at the potentials of the second peak of reduction $[Cobpy]^+ + e^- \rightarrow Co^0$ bpy are often so high that they are difficult to estimate because at high substrate concentrations this wave is superimposed with the reduction wave of the organic halide. Only in the case of 1-bromo-2methylbenzene and 2-chlorothiophene, the second waves increase not so much, and the calculation of k^{II}_{app} becomes possible. The $k^{II}_{app}/mol^{-1} L^{-1} s^{-1}$ values are independent of the substrate concentration, which is characteristic of the first order reactions with respect to organic halide.

It can be assumed that the first stage of the reaction is oxidative addition with the formation of the cobalt σ-complex

 $[Cobpy]^+ + RX \longrightarrow [RCo Xbpy]^+.$

This complex can undergo further transformations, e.g., decomposion, disproportionation, or reduction by [Cobpy]⁺. In some cases, the peak of this intermediate product is detected in voltammograms. For example, a new peak at -1.55 V with $i_p \sim \sqrt{C_{\text{PhI}}}$ is observed for iodobenzene reduction. In the cases of 1-iodohexane and 1-iodo-3-methylbutane, similar peaks at -1.60—-1.66 V first increase and then decrease with an increase in C_{RX} . Probably, this is related to different orders with respect to the substrate for reactions, which occur at this potential. In most cases described earlier for the nickel(II) complexes with bpy and in this work for the cobalt(II) complex with bpy, the currents of the reduction peaks of intermediate products are proportional to the square root of the substrate concentration $i = a_1 \sqrt{C} + b_1$. If the plot of the current of the oxidative addition products vs. substrate concentration is parabolic, then $i = a_2C^2 + b_2C + d$ (a, b, and d are unknown coefficients) with the parabola vertex facing up.

Somewhat different pattern is observed for the reduction of allvl bromide by the electrochemically generated [Cobpy]⁺ complexes unsaturated with bpy. In the presence of allyl bromide, three peaks are observed (the potential of the second peak corresponds to the initial peak) instead of a single peak corresponding to the transformation of [Cobpy]²⁺ into [Cobpy]⁺. The total current corresponding to the two first peaks is much greater than the catalytic currents of the peaks observed in the case of other substrates under similar conditions. It can be assumed that allyl bromide acts as the substrate undergoing reduction at the C-Br bond and also as the ligand

capable of coordinating with the cobalt(II) ion, shifting the reduction wave of the latter to less negative potentials. Such a shift is characteristic of ligands, which form a stronger complex with the reduced form of cobalt. In this case, the unbound form of the Co⁺ complex and the form bound to allyl bromide should be in equilibrium, and each of them can catalytically reduce the substrate. Therefore, the total current characterizing the reduction of allyl bromide at these two first waves was used for the calculation of the k^{II}_{app} value. However, we have to admit that the obtained k^{II}_{app} constant corresponds to a more complicated process than the process for other RX and their comparison is insufficiently correct. We can say that the efficiency of the catalytic regeneration of the cobalt complex in the presence of allyl bromide is much higher. This can be caused by a less strength of the C-Br bond in the latter and its capability of coordinating with the cobalt(II) or cobalt(I) ion, which facilitates reduction.

Preparative reduction of organic halides with the [Cobpy]⁺ complexes. Many key stages of the mechanism of reactions catalyzed by the Co¹ complexes with bpy remain unclear. Therefore, it is of interest to study in detail the routes of RX transformations and the nature of intermediates. We chose PhBr, o-BrC₆H₄Me (o-BrTol), and Me₃C₆H₂Br (MesBr) as model halides. The use of this series of substrates makes it possible to model and compare the routes of reactions involving various intermediates different in stability due to the Me group in the *ortho*-position of the benzene ring.

In the absence of the cobalt complexes, the reduction of RX occurs at high negative potentials (\sim -2.6 V) and the polarographic limiting currents correspond in all cases to the transfer of two electrons per the RX molecule. The reduction products are the corresponding hydrocarbons (RH), and no R—R dimers form. Thus, heterogeneous reduction is a two-electron process

$$RX + 2e + H^+ \longrightarrow RH + X^-$$
.

In all cases except that with MesBr, the preparative reduction of the chosen aryl halides in the presence of the cobalt complexes affords the R-R dimers, which are formally the products of one-electron reduction of RX (Table 3).

It can be assumed that the reaction of the Co^{1} complex with RX proceeds *via* one of the possible mechanisms: (a) outer-sphere mechanism of electron transfer; (b) inner-sphere mechanism including transformations in the coordination sphere of the Co^{1} complex.

The outer-sphere mediator does not bind with substrates in the transition state and works as an electrode (electron source). In this case, the products should be **Table 3.** Products of electrochemical reduction of aryl bromides in the absence and presence of the cobalt complexes with bpy

ArBr	Precursor of catalyst	Product	Product distribution (%)
PhBr	_	PhH	100
	CobpyBr ₂	Ph-Ph	81
	_	PhH	19
o-BrTol	_	TolH	100
	CobpyBr ₂	Tol-Tol	52
	_	TolH	48
MesBr	CobpyBr ₂	MesH	100*

* After acid hydrolysis.

the same as those in heterogeneous reduction (in the absence of adsorption). Therefore, the mechanism of interaction of $[Cobpy]^+$ with RX through oxidative addition is more preferential due to the formation of a considerable amount of the dimeric R—R products (Scheme 2).

Scheme 2

$$[Cobpy_3]^{2^+} + e^- \Longrightarrow [Cobpy_3]^+, \qquad (1)$$

$$[Cobpy_3]^+ \Longrightarrow [Cobpy_2]^+ + bpy, \qquad (2)$$

$$[Cobpy_2]^+ + RX \longrightarrow [RCoXbpy_2]^+, \qquad (3)$$

$$[\mathsf{RCoXbpy}_2]^+ \longrightarrow \mathsf{R}^+ \mathsf{X}^- + [\mathsf{Cobpy}_2]^{2+}, \tag{4}$$

$$2 R' \longrightarrow R-R.$$
 (5)

The absence of dimesityl and MesH in the products of MesBr reduction can be explained by a significant stability of the σ -mesitylcobalt complexes formed in reaction (3) (see Scheme 2). They are completely decompose to MesH in an acidic medium by the treatment of an electrolyte.

In most cases, the $[Cobpy]^+$ complex interacts slowly with RX, which is indicated by the absence of the peak caused by catalyst regeneration and additional peaks corresponding to the reduction of the addition products (σ -organyl complexes) in the CV curves of the current increase.

In order to elucidate whether the target electrosynthesis of σ -organometallic cobalt derivatives is possible, we studied the reduction of the PhBr, *o*-TolBr, and MesBr substrates by [Cobpy]⁺. As mentioned above, under CV conditions the coordinationally saturated complexes are reactive toward these substrates only at potentials of the second peaks of cobalt reduction. Therefore,



Fig. 4. Cyclic voltammogram for $\text{CoBr}_2\text{bpy}(1.7 \cdot 10^{-2} \text{ mol } \text{L}^{-1})$ in the absence (1) and presence (2) of aromatic bromides in DMF.

they will not be considered in this report. The coordinationally unsaturated complexes, including CobpyBr₂, are more reactive. They do not exhibit the current gain, but the reversibility of the first peak disappears, and a new peak appears. The polarization curves of electrochemical reduction of the CobpyBr₂ complex in the absence and presence of PhBr are presented in Fig. 4.

It can be assumed that the peak at the $E_p^{C_3}$ potential corresponds to the reduction of the oxidative addition product, *viz.*, σ -phenylcobalt complex

[Cobpy]⁺ + PhBr → [PhCoBrbpy]⁺.

Its further transformations can be decomposition, disproportionation, or reduction by [Cobpy]⁺.

The oxidation state of cobalt in the oxidative addition product remains unclear. The redox potentials of the initial Co^{II} complex and its reduced Co^I form are different. If the two-electron process occurs during the oxidative addition of Co^I, the Co^{III} complex with a higher redox potential than the initial Co^{II} complex should be formed. However, this is not observed in the voltammograms. Therefore, one-electron oxidation seems to be more preferential. In the case of cobalt, the hydrocarbon R group (at the initial RX molecule) can bind with the metal due to combining electrons (one electron from each fragment), *i.e.*, the R group in the σ -complex is uncharged, and cobalt has the oxidation state 2+, as in the initial Co^{II} complex. In this case, the σ -complex is characterized by free radical reactions rather than nucleophilic reactions of the potentially carbanionic R⁻ group. At the same time, it is well known that these are precisely the radical reactions which are characteristic of compounds with the assumed involvement of Co^{III}.

We carried out the preparative electrolysis of the CobpyBr₂ complex and PhBr (1 : 3) at the potential $E^{C_1} = -1.3$ V in a cell with a magnesium anode. After 1 *F* electricity was passed through the electrolyte, the C₁ and C₃ peaks were still observed in the voltammogram. The current of the C₁ peak somewhat decreased, and the



Fig. 5. Cyclic voltammogram for a solution of CoBr_2 bpy $(1.7 \cdot 10^{-2} \text{ mol } \text{L}^{-1})$ in a DMF solution of Et_4NBF_4 (0.1 mol $\text{L}^{-1})$ in the presence of PhBr $(5.1 \cdot 10^{-2} \text{ mol } \text{L}^{-1})$ before electrolysis (1) and after passing 1 *F* electricity (2).

peaks at E^{C_3} increased compared to the values before electrolysis (Fig. 5).

Further passing electricity until the complete consumption of PhBr does not substantially change the situation. The GLC analysis of the solution showed benzene and biphenyl as the products (19 : 81). Thus, product of oxidative addition, PhCoBr₂bpy, is insufficiently stable under the experimental conditions, and the catalyst regenerates at E^{C_1} .

The preparative reduction of *o*-BrTol by [Cobpy]⁺ (3 : 1) gives similar results. After electrolysis at the E^{C_1} potential (6 *F*) the solution becomes violet, which corresponds to the TolCoBr₂bpy σ -complex formed due to oxidative addition. As in the case of PhBr, all peaks are retained in the CV curves. However, the height of the first peak decreases considerably, and the C₃ peak corresponding to the σ -complex becomes predominant. Thus, the tolyl σ -complex is more stable than the phenyl complex. The complex slowly decomposes in the air, and after 1–2 h a solution of the electrolyte becomes green. It can be assumed that CobpyBr₂ forms. This assumption is confirmed by the voltammetric data. The chromatographic analysis of the solution showed toluene and ditolyl (48 : 52) as the products.

The stability of the aryl σ -complexes containing the Me group in the *ortho*-position of the aromatic ring is due to steric factors preventing rotation around the σ -Ar—Co bond and the axial attack of the reactants at the cobalt atom.¹⁰ Therefore, it is reasonable to choose MesBr with two Me groups in the *ortho*-position for the synthesis of more stable σ -complexes. For example, the combined electrochemical reduction of CobpyBr₂ and MesBr was carried out in a divided cell. After the end of





Fig. 6. Cyclic voltammogram for a solution of [MesCoBr₂bpy] (0.01 mol L^{-1}), *viz.*, product of the combined electrolysis of CoBr₂bpy and MesBr, in DMF (after passing 1.2 *F* electricity).

electrolysis (complete disappearance of the reduction peak of the initial complex at ~-1.3 V, ~1.2 *F* electricity per Co atom were passed), the voltammogram of the solution exhibited one reversible one-electron wave at more negative potentials ($E^{C_3} = -1.75$ V) (Fig. 6), which can be attributed to the reduction wave of the σ -mesitylcobalt complex formed according to Scheme 3.

Scheme 3

[Cobpy]⁺ + MesBr → [MesCobpyBr]⁺,

[MesCobpyBr]⁺ + e[−] → MesCobpyBr.

This complex was isolated from a solution and characterized by spectroscopy and elemental analysis.

Note that the occurrence of two Me groups in the *ortho*-position inhibits not only reductive elimination but also other possible reactions, for example, oxidative addition involving the σ -mesityl complex. The GLC analysis of the ether extract of the reaction mixture showed only traces of MesH as the products of MesBr transformation (because the major portion of MesH is bound to the stable σ -mesityl complex), and after acid hydrolysis MesH formed in almost 100% yield.

Thus, the formation of cobalt organic σ -complexes, which are poorly studied compounds, was shown. Compounds with this structure are key intermediates for the whole series of reactions. However, they decompose, as

a rule, during isolation. The metal—carbon bond is very reactive, and only several organometallic cobalt complexes are known to date. In some cases, the σ -complexes can be isolated and studied independently as model compounds in the investigation of mechanisms of organometallic synthesis.

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