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Electrochemical arylation of cobalt and nickel chelates with diphenyliodonium salts

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Electrochemical arylation of cobalt chelates with diphenyliodonium salts occurs at low cathodic potentials (*viz.*, potential of the first reduction wave of the diphenyliodonium salt) and affords the phenyl derivatives of Co^{III} chelates containing the σ-Co—C(sp^2) bond. Nickel complexes should be arylated at higher cathodic potentials because it is necessary to generate paramagnetic Ni^I complexes.

Key words: cobalt, nickel, chelates, diaryliodonium salts, arylation, electrochemical activation.

Transition metal chelates are known as systems modeling active sites of several natural metal enzymes and as catalysts for many organic reactions, *viz.*, alkylation, acylation, homo- and cross-coupling, and others (see, *e.g.*, Ref. 1 and literature cited therein). The catalytic process often produces intermediate compounds containing σ-metal—carbon bonds, which further serve as the carriers of alkyl, aryl, alkenyl, acyl, and other groups to an organic substrate. In this connection, the synthesis and study of the properties of such organometallic intermediates are of interest.

Three main approaches[2] were developed for the synthesis of organocobalt compounds containing the covalent Co—C bond: reactions of Co^{III} complexes with nucleophiles, reactions of Co^{II} complexes with radicals, and reactions of Co^I complexes with electrophiles.

Syntheses of mono- and dialkyl Co^{III} derivatives using each of these approaches are widely exemplified in the literature.[3—5] Syntheses of aryl and vinyl organocobalt compounds are much more rare.[6—11]

Great attention is given to a combination of organic electrosynthesis with catalysis by transition metal complexes. Complexes of low-valence transition metals, for example, supernucleophilic anions containing Co^I or Ni^I, are easily generated electrochemically and are capable of reacting *in situ* with many organic substrates to form compounds with the σ-carbon—metal bonds, which in turn can be carriers of an organic group to the second organic or inorganic reactant present in a solution.[12—18]

Electrochemical alkylation[19—28] of the Co complexes has been studied in rather detail. Meanwhile, data for the Ni complexes are scarce. In these reactions supernucleophiles, such as anionic Co^I complexes, are electrochemically generated and then are introduced *in situ* into the reaction with alkyl halides or methylcobaloxime. The aryl and alkyl Co^{III} complexes are reduced at much higher cathodic potentials than those of their precursors,[29] Co^{II} complexes containing no Co—C bond. Therefore, it is possible to electrochemically generate anions of the Co^I complexes by electrolysis at a controlled potential with no risk of the subsequent destructive reduction of the reaction product. The situation is more complicated for the nickel complexes.

There is a basic distinction between the anionic Co^I and Ni^I chelates: the Co^I anions are even-electron with the 16-electron valent metal shell (ignoring axial ligands, *e.g.*, solvent molecules), whereas the Ni^I anions are odd-electron with the 17-electron valent shell. Therefore, it can be expected that the Ni^I compounds react preferentially with alkylating agents, *viz.*, radical precursors. This reactant is, *e.g.*, methylcobaloxime $MeCo^{III}(dmgH)_2$:[28]

$$\begin{tikzcd}
\mathrm{MeCo^{III}(dmgH)_2} & + & {[(\mathrm{Chel})_2\mathrm{Ni^{I}}]^-} \arrow[r] & {[(\mathrm{Chel})_2\mathrm{Ni^{II}Me}]^-} \arrow[d, "-e"] & + & \mathrm{Co^{II}(dmgH)_2} \\
 & & (\mathrm{Chel})_2\mathrm{Ni^{II}} \arrow[u, "+e"'] & (\mathrm{Chel})_2\mathrm{Ni^{III}Me} & &
\end{tikzcd}$$

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In the case of alkyl halides, the probability of the single electron transfer (SET) mechanism increases:

$$[(\mathrm{Chel})_2\mathrm{Ni^I}]^- + \mathrm{RHal} \longrightarrow [(\mathrm{Chel})_2\mathrm{Ni^{II}}] + \mathrm{R}^{\bullet} + \mathrm{Hal}^-,$$

$$[(\mathrm{Chel})_2\mathrm{Ni^I}]^- + \mathrm{R}^{\bullet} \longrightarrow [(\mathrm{Chel})_2\mathrm{Ni^{II}R}]^-,$$

$$[(\mathrm{Chel})_2\mathrm{Ni^{II}R}]^- - \mathrm{e} \longrightarrow [(\mathrm{Chel})_2\mathrm{Ni^{III}R}].$$

Unlike the Co^{II} complexes, the nickel complexes used as catalysts are divided into two groups. The first group contains the Ni^{II} complexes that are immediately reduced electrochemically to the corresponding zero-valence species in one reversible two-electron stage (*viz.*, Ni^{II} complexes with bpy, phen, PPh$_3$, or dppe). The second group represents the complexes that are reduced stepwise through the intermediate formation of Ni^{I}, which transforms into Ni^0 at much more cathodic potentials (*e.g.*, Ni^{II} complexes with cyclames, salenes, as well as dmgH, and sulfur-containing chelating ligands studied in this work).[24] The distinction in behavior of these complexes in the presence of organic halides is that the complexes of the first group, being reduced to the Ni^0 compounds, loose one of their ligands and react with RHal or ArHal *via* the oxidative addition route, for example,

$$[(\mathrm{bpy})_2\mathrm{Ni^{II}}]^+ + 2\mathrm{e}^- \longrightarrow (\mathrm{bpy})\mathrm{Ni^0} + \mathrm{bpy},$$

$$(\mathrm{bpy})\mathrm{Ni^0} + \mathrm{ArHal} \longrightarrow \mathrm{ArNi^{II}(bpy)Hal}.$$

Electrochemically activated arylation reactions of the cobalt and nickel complexes were not studied earlier. The purpose of this work is to develop methods for the introduction of the phenyl group in various Co^{II}, Co^{III}, and Ni^{II} chelates using electrochemically generated phenyl radicals. The diaryliodonium salts Ph$_2$IBF$_4$, Ph$_2$IBr, and (p-t-Bu-C$_6$H$_4$)$_2$IBF$_4$ served as the source of aryl radicals.

Experimental

Instruments and electrodes. Electrochemical reduction potentials were measured using a PI-50-1.1 potentiostat, a PR-8 programmer, and a PDA-1 two-coordinate recorder on a stationary and rotating platinum electrode with a working surface area of 5.14 mm^2 in a 0.05 *M* solution of n-Bu$_4$NBF$_4$ at 20 °C in a special electrochemical cell in anhydrous MeCN.

Cyclic voltammetry (CVA) curves were recorded on a stationary Pt electrode at a sweep of 200 mV s^{-1}. The electrode was thoroughly cleaned by polishing after recording each curve.

Preparative electrolysis was carried out using a P-5827M potentiostat in an electrolytic cell with separated anodic and cathodic spaces on an electrode from a graphite tissue (surface area 2.29 cm^2) in the presence of n-Bu$_4$NBF$_4$ (0.05 mol L^{-1}) as a supporting electrolyte in anhydrous acetonitrile at 20 °C.

In all the cases, platinum served as an auxiliary electrode, and a saturated Ag/AgCl electrode was used as a reference.

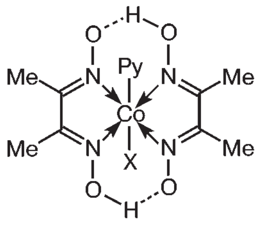
Starting compounds and reagents. The Co^{II} and Co^{III} dimethyl glyoximate complexes were synthesized according to known procedures.[30,31] The Co and Ni complexes with sulfur-containing ligands* based on α-thiopicolinamides were synthesized according to a previously published method.[32] Diphenyliodonium was prepared by a known procedure.[33] n-Bu$_4$NBF$_4$ (Aldrich) was used.

Acetonitrile (reagent grade) was stirred for 24 h above CaH$_2$ and filtered. KNO$_3$ (5 g) and concentrated H$_2$SO$_4$ (3 mL) were added, and the resulting mixture was refluxed for 3 h and distilled. After this, MeCN was refluxed for 2 h above P$_2$O$_5$ and distilled, collecting the fraction with b.p. 81—82 °C. The concentration of solutions of the studied compounds was $(3\text{—}5) \cdot 10^{-4}$ mol L^{-1}.

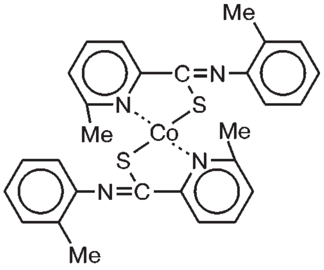
Preparative electrolysis (general procedure). Electrolysis at a controlled potential was conducted in a 10-cm^3 cell in MeCN with 0.05 *M* n-Bu$_4$NBF$_4$ solution. Weighted samples of the chelate ($5 \cdot 10^{-4}$ mol) and Ph$_2$I$^+$BF$_4$$^-$ (0.08 g, $1 \cdot 10^{-3}$ mol) were dissolved in MeCN (10 mL) and subjected to electrolysis at the potential of the first wave reduction of Ph$_2$I$^+$BF$_4$$^-$. To remove dioxygen and to stir the electrolyte solution, argon saturated with a solvent vapor was passed through the cell. The completeness of electrolysis was concluded from a drop of current passing through the system. Electrolysis was stopped when the current became at most 10—15% of the initial value. The obtained solution was studied by CVA on a platinum electrode.

Results and Discussion

The Co^{II}, Co^{III}, and Ni^{II} complexes with chelating ligands containing N and S atoms were chosen for investigation.



(dmgH)$_2$CoPyX (X = Py, Cl)



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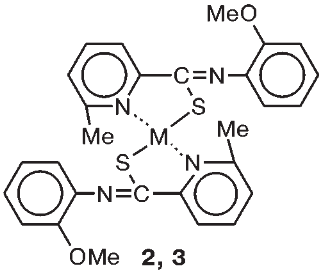

2, 3

M = Co (**2**), Ni (**3**)

The electrochemical properties of the Co dimethyl glyoximate complexes are well known,[34] whereas the electrochemical behavior of sulfur-containing complexes

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* The Co and Ni complexes with sulfur-containing ligands were kindly presented by I. G. Il´ina.

based on α-thiopicolinamides **1—3** has been studied recently.[28] The reduction of these compounds involves orbitals localized on the metal:

$$\mathrm{Co^{III}(Chel)_2X \xrightarrow[-X]{+e} Co^{II}(Chel)_2 \overset{+e}{\rightleftharpoons} [Co^{I}(Chel)_2]^-},$$

$$\mathrm{Ni^{II}(Chel)_2 \overset{+e}{\rightleftharpoons} [Ni^{I}(Chel)_2]^-}.$$

According to the CVA data, the potentials of the $\mathrm{Co^{II}/Co^{III}}$ and $\mathrm{Co^{II}/Co^{I}}$ redox transitions fall within the intervals from −0.6 to −0.7 V and from −1.08 to −1.28 V, respectively (*vs.* Ag/AgCl/KCl(sat.)). For the studied $\mathrm{Ni^{II}}$ α-thiopicolinamide complex, the $\mathrm{Ni^{II}/Ni^{I}}$ redox transition is observed at a potential of −1.38 V (Table 1).

Table 1. Potentials of reduction peaks of the initial Co and Ni chelates and reaction mixtures obtained by preparative electrolysis of these complexes in the presence of $\mathrm{Ph_2IBF_4}$ or $(p\text{—}\mathrm{Bu^t\text{-}C_6H_4)_2IBF_4}$

Compound or mixture	$-E^{\mathrm{red}}$/V
$\mathrm{(dmgH)_2CoPy_2}$	1.08, 2.10
$\mathrm{Ph_2IBF_4}$	0.58, 2.02
$\mathrm{(dmgH)_2CoPy_2}^{a}$ + $\mathrm{Ph_2IBF_4}^{b}$	0.65, 1.10, 1.56^{c}, 2.05
$(p\text{-}\mathrm{Bu^t\text{-}C_6H_4)_2IBF_4}$	0.60, 2.06
$\mathrm{(dmgH)_2CoPy_2}^{a}$ + $(p\text{-}\mathrm{Bu^t\text{-}C_6H_4)_2IBF_4}^{b}$	0.60, 1.08, 1.62^{c}, 2.10
1	1.28, 1.80
1^{a} + $\mathrm{Ph_2IBF_4}^{b}$	0.60, 1.18, 1.66^{c}, 1.83
2	1.20, 1.96
2^{d} + $\mathrm{Ph_2IBF_4}^{b}$	0.70, 1.20, 1.68^{c}, 2.00
2^{d} + $\mathrm{Ph_2IBF_4}^{b}$ after preparative electrolysis at −0.8 V	0.68, 1.68^{c}
3	1.38, 2.02
3^{d} + $\mathrm{Ph_2IBF_4}^{b}$ after preparative electrolysis at −1.4 V	1.66^{c}
$\mathrm{(dmgH)_2CoPyCl}$	0.68, 1.10, 1.96
$\mathrm{(dmgH)_2CoPyCl}^{a}$ + $\mathrm{Ph_2IBF_4}^{b}$	0.72, 1.10, 1.54^{c}, 2.01
$\mathrm{(dmgH)_2CoPyCl}^{a}$ + $\mathrm{Ph_2IBF_4}^{b}$ after preparative electrolysis at −0.8 V	0.71, 1.54^{c}
$\mathrm{(dmgH)_2CoPyCl}^{a}$ + $(p\text{-}\mathrm{Bu^t\text{-}C_6H_4)_2IBF_4}^{b}$ after preparative electrolysis at −0.8 V	0.70, 1.64^{c}
$\mathrm{(dmgH)_2PhCoPy}$	1.56

Note. Electrolysis was conducted on the Pt electrode in MeCN in the presence of a 0.05 *M* solution of $\mathrm{Bu_4NBF_4}$. The potential values are presented relatively to Ag/AgCl/KCl(sat.).

Concentrations of solutions/mol $\mathrm{L^{-1}}$: [a] $2 \cdot 10^{-4}$; [b] $1 \cdot 10^{-3}$; [d] $1 \cdot 10^{-4}$.

[c] The potentials correspond to the reduction of the electrolysis products, *viz.*, aryl $\mathrm{Co^{III}}$ and $\mathrm{Ni^{III}}$ complexes containing the σ-M—C($\mathrm{sp^2}$) bond.

The diphenyliodonium salts are also reduced stepwise.[35] The first reduction peak is observed at −0.6 V.

$$\mathrm{Ph_2I^+X^- + e^- \longrightarrow Ph^{\bullet} + PhI + X^-}$$

The further transformations of the primarily formed phenyl radicals are determined mainly by the composition of the solution. The presence in the reaction mixture of compounds capable of fast reacting with phenyl radicals decreases substantially the contribution of further reduction of radicals on the electrode and abstraction of the hydrogen atom from the solvent. The second peak corresponding to the reduction of iodobenzene appears at a potential of −2.02 V (*vs.* Ag/AgCl/KCl(sat.)).

Thus, if a reaction mixture containing paramagnetic $\mathrm{Co^{II}}$ or $\mathrm{Ni^{I}}$ chelates, which react readily with radicals, contains a diphenyliodonium salt, its one-electron reduction can initiate arylation, for example, according to Schemes 1 and 2.

Scheme 1

$$\mathrm{Ph_2I^+ + e^- \longrightarrow Ph^{\bullet} + PhI},$$

$$\mathrm{Ph^{\bullet} + (Chel)_2Co^{II} \longrightarrow (Chel)_2PhCo^{III}}.$$

Scheme 2

$$\mathrm{Ph_2I^+ + e^- \longrightarrow Ph^{\bullet} + PhI},$$

$$\mathrm{(Chel)_2Ni^{II} + e^- \longrightarrow [(Chel)_2Ni^{I}]^-},$$

$$\mathrm{[(Chel)_2Ni^{I}]^- + Ph^{\bullet} \longrightarrow [(Chel)_2Ni^{II}Ph]^-},$$

$$\mathrm{[(Chel)_2Ni^{II}Ph]^- - e^- \longrightarrow (Chel)_2Ni^{III}Ph}.$$

Organometallic complexes with the $\mathrm{Ni^{III}}$—C bond are kinetically unstable and easily dissociate through a cleavage of the metal—carbon bond ($\mathrm{Ni^{III}\text{—}R \longrightarrow Ni^{II} + R^{\bullet}}$). Stability of these compounds depends strongly on the nature of polydentate ligands bound to the metal (see, *e.g.*, Ref. 34 and literature cited therein). For instance, the anionic $[2,6\text{-}(\mathrm{Me_2NCH_2)C_6H_3}]^-$ ligand stabilizes the $\mathrm{Ni^{III}}$ organometallic compounds[36—38] and strongly decreases the redox potential of the $\mathrm{Ni^{II}/Ni^{III}}$ pair.[39] The formation of low-stability compounds with the $\mathrm{Ni^{III}}$—C bonds as intermediates is postulated by many authors[34,40—45] in metallocomplex catalysis and biology. The data presented below show that the complex with the $\mathrm{Ni^{III}}$—Ph bond obtained from compound **3** is rather stable in the CVA time scale.

The CVA curves for all studied mixtures containing the $\mathrm{Co^{II}}$ complex and $\mathrm{Ph_2I^+X^-}$ (two- to fivefold excess of the latter) exhibit the appearance of a low-intensity peak in the potential region from −1.5 to −1.7 V (*vs.* Ag/AgCl/KCl(sat.)) already at the first scan. This peak

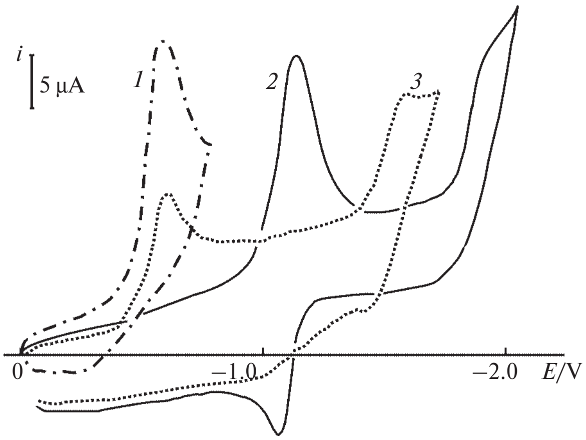

Fig. 1. Cyclic voltammograms for Ph_2IBF_4 ($2 \cdot 10^{-4}$ mol L^{-1}, *1*), $(dmgH)_2CoPy_2$ ($2 \cdot 10^{-4}$ mol L^{-1}, *2*), and resulting mixture obtained after preparative electrolysis at −0.8 V (Pt, MeCN, *vs.* Ag/AgCl/KCl(sat.), *3*).

corresponds to the reduction of the arylated complexes (see Table 1).

Preparative electrolysis of these mixtures at the potential of diphenyliodonium reduction (−0.6 V) results in the appearance of a compound characterized by the cathodic peak in the same potential region (−1.5 to −1.7 V) (see Table 1, Fig. 1). The graphite tissue with the high specific surface area was used as a working electrode in electrolysis because a platinum electrode is rapidly passivated. We showed that the reduction potentials of the starting compounds slightly change when the platinum material of the working electrode is replaced by graphite.

In order to prove the assignment of the cathodic peaks (E = −1.5—−1.7 V), we synthesized the $(dmgH)_2PhCoPy$ complex by the reaction of the Co^{III} complex with the Grignard reagent:

$$(dmgH)_2CoPyCl + PhMgBr \longrightarrow$$
$$\longrightarrow (dmgH)_2PhCoPy + MgBrCl.$$

It turned out that the CVA curves for a solution of the authentic complex contain the characteristic irreversible cathodic peak at a potential −1.56 V, which coincides in position with the potential of the cathodic peak of the product of electrochemical arylation. The potentials of peaks of the electrolysis products and a solution of the $(dmgH)_2PhCoPy$ complex in the anodic branch of the cyclic voltammogram also coincide.

Thus, for the reaction of the Co^{II} complexes with diphenyliodonium salts, it is enough to activate electrochemically only one of these reactants. The active phenyl radicals generated by the reduction of Ph_2I^+ react rapidly with the Co^{II} complex (see Scheme 1).

Diphenyliodonium salts with various substituents in the benzene ring can also be introduced into the reaction. For example, preparative electrolysis of a mixture of $(p\text{-}Bu^tC_6H_4)_2IBF_4$ with the Co dimethyl glyoximate complex affords the corresponding aryl derivatives, whose reduction potential is a little shifted to the cathodic region compared to that of $PhCo(dmgH)_2Py$ (see Table 1).

The above arylation reaction can involve not only Co^{II} but also Co^{III} complexes, which, as a rule, are more stable and accessible. However, in this case, both participants of the reaction need electrochemical activation, *i.e.*, generation of the aryl radicals from the diphenyliodonium salt and reduction of Co^{III} to the paramagnetic Co^{II} complex. The value of the controlled electrolysis potential remains virtually unchanged. This is related to the fact that the Co^{III}/Co^{II} redox transition for the most of complexes occurs in a potential range of −0.4—−0.8 V (*vs.* Ag/AgCl/KCl(sat.)), *i.e.*, very close to the reduction potential of the iodonium salts. Therefore, at specified potential values, we can simultaneously generate $Ph^{\bullet}$ and the Co^{II} complex, which then react with each other *in situ*.

Our studies showed that electrolysis of reaction mixtures containing the Co^{II} or Co^{III} dimethyl glyoximate complexes gives the same arylation product, namely, $(dmgH)_2PhCoPy$ (Scheme 3, see Table 1).

Scheme 3

$$(dmgH)_2Co^{III}PyCl + e^- + MeCN \longrightarrow$$
$$\longrightarrow (dmgH)_2Co^{II}Py(MeCN) + Cl^-,$$
$$Ph_2I^+BF_4^- + e^- \longrightarrow Ph^{\bullet} + PhI + BF_4^-,$$
$$(dmgH)_2Co^{II}Py(MeCN) + Ph^{\bullet} \longrightarrow$$
$$\longrightarrow (dmgH)_2PhCo^{III}Py + MeCN.$$

Preparative electrolysis of the sulfur-containing cobalt and nickel chelates in a mixture with $Ph_2I^+BF_4^-$ also produces compounds with reduction peaks at potentials of −1.66 and −1.68 V, respectively, which indicate arylation to occur (see Table 1). This is characteristic of compounds containing the σ-Co—C and Ni—C bonds.

However, nickel complex **3** is arylated only at the potential of the first reduction wave (−1.38 V), *i.e.*, the paramagnetic Ni^I complex reacts with phenyl radicals. The initial diamagnetic Ni^{II} complex, unlike the paramagnetic Co^{II} compounds, reacts very slowly. The arylation product is not formed by preparative electrolysis of a mixture of diphenyliodonium borofluoride and complex **3** at the potential of the first wave of Ph_2IBF_4 reduction.

The preparative electrolysis of a mixture of the ligand from complexes **2** or **3** and diphenyliodonium borofluoride at the reduction potential of the latter produces a compound, which is reduced at potentials being 120 mV less cathodic than that of the arylation product, *e.g.*, complex **2**. This indicates that the arylation of the chelate results in the formation of the σ-carbon—metal bond rather than ligand arylation. In addition, if complex **2** is arylated at the S atoms, the reaction product would be the Co^{I} complex, which is reduced at much more cathodic potentials (about −2.0 V *vs*. Ag/AgCl/KCl(sat.)), which was not in fact found.

The obtained results show a possibility of electrochemical arylation of the Co^{II}, Co^{III}, and Ni^{II} chelates with diphenyliodonium salts. In the case of the cobalt complexes, the reaction occurs at low cathodic potentials (potential of the first wave of diphenyliodonium salt reduction) and results in the formation of phenyl derivatives of the Co^{III} chelates containing the σ-Co—C(sp^2) bond. The application of diphenyliodonium salts as arylating agents has a doubtless advantage over such traditionally used in $S_{RN}1$ reactions reagents as halobenzene because the generation of phenyl radicals due to their electroreduction occurs at much lower cathodic overvoltages.

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