CHEMISTRY
A EUROPEAN JOURNAL

Co^I- and Co^0-Bipyridine Complexes Obtained by Reduction of $CoBr_2$bpy: Electrochemical Behaviour and Investigation of Their Reactions with Aromatic Halides and Vinylic Acetates

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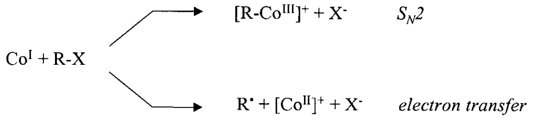
Abstract: The electrochemical behaviour of $CoBr_2$bpy (bpy = 2,2′-bipyridine) catalyst precursor in acetonitrile has been studied, revealing its possible reduction into the corresponding Co^I and Co^0 complexes. These low-valent cobalt species appear to be stable on the time scale of cyclic voltammetry. In the presence of aromatic halides, both complexes undergo oxidative addition, the latter Co^0 species allowing the activation of poorly reactive aromatic chlorides. The arylcobalt^{III} and arylcobalt^{II} obtained are reduced at the same potential as the original Co^{II} and Co^I complexes, respectively, resulting in the observation of overall ECE mechanisms in both cases. The electrochemical study shows that vinylic acetates competitively react with electrogenerated Co^0 species, leading to a labile complex. Preparative scale electrolyses carried out from solutions containing aromatic halides (ArX), vinyl acetate (vinylOAc) and a catalytic amount of $CoBr_2$bpy lead to a mixture of biaryl (Ar-Ar) and arene (ArH) as long as the potential is set on the plateau of the $Co^{II} \rightleftarrows Co^I$ reduction wave. The coupling product (Ar-vinyl) is formed only if the electrolysis is performed on the plateau of the Co^I/Co^0 reduction wave. A mechanism is proposed for the overall cobalt-catalyzed coupling reaction between aromatic halides and allylic acetates.

Keywords: cobalt • halides • kinetics • vinylation

Introduction

The organometallic chemistry of cobalt has mainly focused on the activation of alkyl halides by stable macrocyclic cobalt(I) complexes. Indeed, vitamin B_{12} derivatives,[1] cobalt porphyrins[2] have received much attention owing to their high nucleophilicity towards organic electrophiles. Mechanistic investigations involving such complexes[3] or their cobalt–salen analogues,[4,5] have established that Co^I may undergo either oxidative addition on alkyl halides (S_N2 mechanism) or electron transfer with the release of $R^•$, X^-, and Co^{II}-depending on both the nature of the leaving group X and the degree of substitution of the alkyl moiety, as depicted below.



However, strong C–X bonds such as those met in aromatic bromides or chlorides are not activated by these stable Co^I species. In fact, their synthetic applications mainly concern alkyl halides,[4,6,7] α-haloesters or α-haloketones.[5] In that context, the quest for reactive low-valent cobalt complexes within the scope of C–C bond formation has become a major topic in our group. Over the past five years, we have focused on cobalt-centered catalytic systems based on the association of a cobalt(II) halide with weak labile complexing agents such as pyridine,[8] allyl ethers[9] or acetates,[10] vinyl acetates,[11] $ZnBr_2$ salts,[12] or mixtures of them. These systems have found applications in both the chemical and electrochemical conversion of aromatic halides into the corresponding arylzinc species,[13,14] or their coupling with aromatic halides,[15] olefins,[16] vinylic acetates.[17]

However, our electroanalytical studies[8] have shown that the increase in reactivity obtained is counterbalanced by the competitive disproportionation of electrogenerated Co^I (see below), which in several examples (aromatic chlorides, namely) proceeds faster than oxidative addition.

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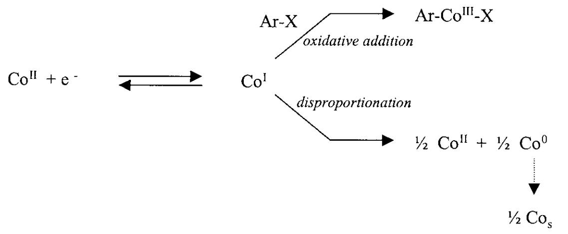
DOI: 10.1002/chem.200400971



Therefore, the design of cobalt catalysts with the highest versatility towards the activation of aromatic halides amounts to finding a good compromise between stability and reactivity. So, cobalt–bipyridine complexes have been successfully used as catalysts in our group for the electrochemical[17] and chemical[18] vinylation of aromatic halides (including aromatic chlorides). $CoBr_2$ and 2,2′-bipyridine are introduced in equimolar amounts in the latter chemical process, which is an unusual metal/ligand stoichiometry with respect to a former work by Margel and Anson[19] where $Co(bpy)_3(ClO_4)_2$ was the catalyst precursor allowing the electroreduction of allyl chloride. The very interesting synthetic applications of $CoBr_2$bipy prompted us to determine the cobalt species actually formed in the first steps of our vinylation process, especially those involved in the activation of aryl chlorides. The use of cobalt–bipyridine complexes for the electrocatalytic reduction of organic halides has been reported by a Russian group.[20] Although the authors mention the dependence of the reactivity of low-valent cobalt species on the bpy/cobalt stoichiometry, their paper mostly focuses on synthetic applications rather than mechanistic aspects.

In the present work, we have examined the electrochemical behaviour of $CoBr_2$bipy in acetonitrile at Pt electrodes in the presence of aromatic halides (Ar-X) and vinylic acetates (vinylOAc). Cyclic voltammetry has been used to characterize the low-valent cobalt species (Co^I and Co^0) obtained by electroreduction of $CoBr_2$bipy, as well as the intermediates formed with Ar-X and vinylOAc. Preparative scale electrolyses have been performed in order to determine the influence of the potential applied on product distribution. A mechanism is proposed, based on the results of both voltammetry and electrolyses, along with kinetic considerations.

Results and Discussion

Electrochemical properties of $CoBr_2$bpy: Figure 1 displays the voltammograms of $CoBr_2$bpy at a Pt electrode in acetonitrile.

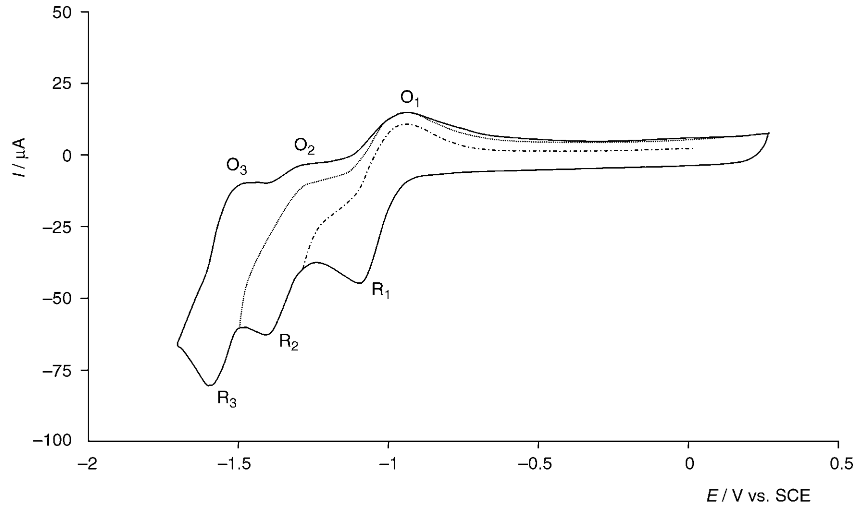


Figure 1. Cyclic voltammograms of $CoBr_2$bpy (5 mM) in an acetonitrile solution containing 0.1 M $TBABF_4$. Electrode: Pt (2 mm diameter). Scan rate: 0.2 $V\,s^{-1}$. Solid lines: inversion potential −1.7 V. Dashed lines: inversion potential −1.5 and −1.3 V.

As shown in Figure 1, $CoBr_2$bpy exhibits three reduction waves, denoted R_1 (−1.03 V), R_2 (−1.35 V) and R_3 (−1.59 V). Three related oxidation waves (O_1, O_2, and O_3, respectively) are observed at the reverse scan. The rather broad-shaped peaks suggest that chemical steps are associated with the electron transfers. Moreover, the three reduction waves could be ascribed either to three successive electron transfers or to the reduction of several distinct complexes resulting from the dissolution of $CoBr_2$bpy in acetonitrile. In order to clear up that point, we have determined the absolute number of electrons exchanged in the process in peak R_1, through the combination of stationary and transient electrochemical techniques, according to a method developed by Amatore.[21] Linear sweep voltammetry at an ultramicroelectrode (25 µm diameter) was used as the stationary technique whereas transient currents were obtained from chronoamperometry. Our calculations led to the following results:

Number of electrons at R_1: $n = 1.08 \pm 0.05$

and a diffusion coefficient of the original Co^{II} species of $D = 8(\pm 1) \times 10^{-6}\ cm^2 s^{-1}$

These results are consistent with a monoelectronic reduction of a single species on the level of R_1. Since R_2 and R_3 exhibit comparable peak currents (as are the stationary currents at R_1 and R_2 in Figure 3), it can be reasonably assumed that three successive monoelectronic waves are observed at R_1,

R_2 and R_3. In that context, the species obtained at R_1 and R_2 formally correspond to Co^I and Co^0, respectively. The rather reversible, monoelectronic reduction observed at R_3 is therefore ascribed to the $Co^0/(Co^0)^{\cdot-}$ couple. In order to further characterize the nature of the complexes of Co^{II}, Co^I and Co^0, we have examined the effect of bromide concentration on the voltammograms obtained for $CoBr_2bpy$. Indeed, $CoBr_2bpy$ could either exist as a molecular (neutral) complex, or dissociate into a cationic moiety and bromide anions. Secondly, one must consider that bromide ions could be exchanged both at R_1 and R_2.

The first point has been investigated through the voltammograms recorded for various concentrations of dry tetrabutylammonium bromide (TBABr) in acetonitrile. Bromide ions exhibit two oxidation waves at 0.78 V ($3Br^- \rightleftarrows Br_3^- + 2e^-$) and 1.13 V ($2Br^- \rightleftarrows Br_2 + 2e^-$) which peak currents are i) in a 2:1 ratio ii) proportional to the concentration of TBABr (Figure 2). The introduction of $CoBr_2bpy$ in an acetonitrile solution containing TBABr has no effect on the voltammograms of Figure 2. Hence, no bromide is either released or added to the cobalt complex, which remains in its initial stoichiometry in acetonitrile.

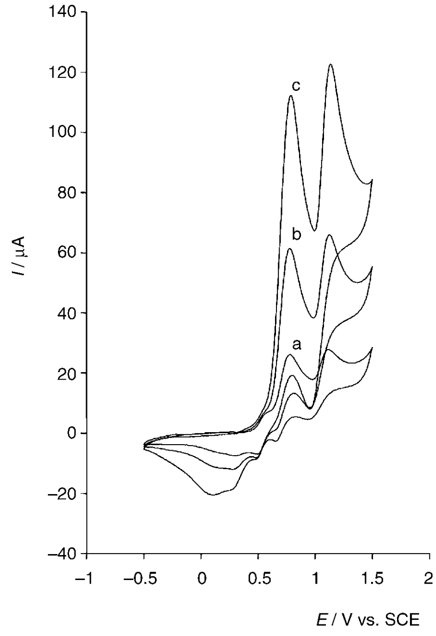


Figure 2. Cyclic voltammograms of TBABr solutions in acetonitrile containing 0.1 M $TBABF_4$. electrode: Pt (2 mm diameter). Scan rate: 0.1 Vs^{-1}. a) [TBABr] = 0.005 M; b) [TBABr] = 0.015 M; c) [TBABr] = 0.025 M;

The influence of bromide concentration on waves R_1 and R_2 has been investigated by rotating disk voltammetry. Figure 3 shows the voltammograms obtained for $CoBr_2bpy$ at various TBABr concentrations, and the variation of the half-wave potential of R_1 and R_2 as a function of the co-logarithm of [TBABr].

The stationary curves displayed in Figure 3 are strongly affected by bromide concentration. Indeed, R_1 and R_2 are similarly shifted toward more negative potentials when bromide concentration increases. A closer examination reveals that half-wave potentials are linear functions of the logarithm of bromide concentration and are shifted by about 60 mV per decade of concentration for both waves. Such behaviour is consistent with the exchange of one bromide ion at each wave.

However, it is unlikely to observe a concerted process including both bromide exchange and electron transfer. Such a sequence must proceed through two distinct steps, the loss of one bromide—although fast—occurring prior to the reduction of Co^{II}. The same feature should apply to the reduction of Co^I as well.

So, considering that the original Co^{II} complex is $CoBr_2$-bpy, the successive steps observed by cyclic voltammetry are summarized below.

$$Co^{II}Br_2bpy \rightleftharpoons Co^{II}Brbpy^+ + Br^-$$

$$Co^{II}Brbpy^+ + e^- \rightleftharpoons Co^IBrbpy \quad R_1\ (-1.03\,V)$$

$$Co^IBrbpy \rightleftharpoons Co^Ibpy^+ + Br^-$$

$$Co^Ibpy^+ + e^- \rightleftharpoons Co^0bpy \quad R_2\ (-1.35\,V)$$

$$Co^0bpy + e^- \rightleftharpoons Co^0bpy^{\cdot-} \quad R_3\ (-1.59\,V)$$

Note that acetonitrile molecules are most likely coordinated to these cobalt complexes, although they do not appear in the equations, for easier representation.

Thus, soluble Co^I- and Co^0–bipyridine complexes are observed at the time scale of voltammetry. However, quantitative electrolyses carried out on the plateau of R_1 in a two-compartment cell engage 2 Faraday per mol of $CoBr_2bpy$, together with the passivation of the gold cathode. So, Co_s is formed on the level of R_1 at the time scale of preparative electrolysis (ca. 10–15 mn), suggesting that electrogenerated Co^Ibpy^+ undergoes disproportionation, which results in the observation of an overall sum of $1 + {}^1\!/_2 + {}^1\!/_4 + {}^1\!/_8 \ldots = 2$ electrons engaged at R_1. Co^Ibpy^+ is therefore unstable, and is only observed at short time scales. Accordingly, soluble Co^0–bpy formed at R_2 should exhibit a poor stability as well, and none of these low-valent cobalt complexes can be neither prepared nor stored long enough to carry out the step by step electrolyses which would allow the separation and full characterization of the intermediate cobalt/organocobalt species that are discussed in the following.

Electrochemical behaviour of $CoBr_2bpy$ in the presence of aromatic halides: Cyclic voltammograms of $CoBr_2bpy$ have been recorded in the presence of various excesses of aromatic bromides and chlorides. Typical voltammograms are represented in Figure 4 for a) ethyl 4-iodobenzoate, b) ethyl 4-bromobenzoate, and c) methyl 4-chlorobenzoate. Al-

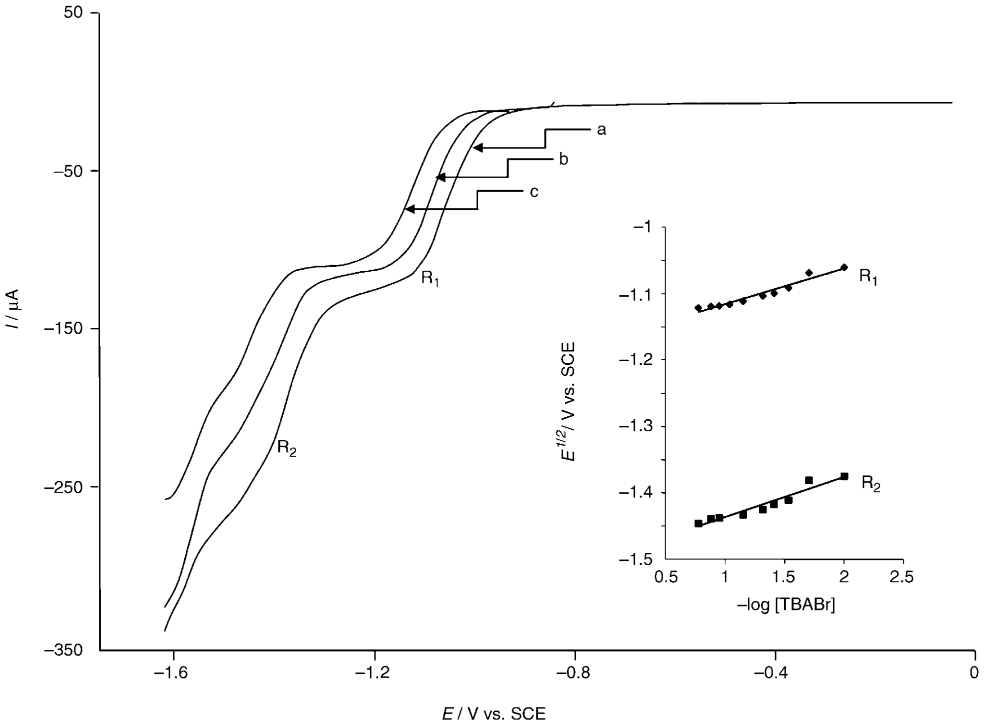


Figure 3. Stationary voltammograms of $CoBr_2bpy$ 0.005 M in acetonitrile (containing 0.1 M $TBABF_4$) in the presence of TBABr. Electrode: RDE Pt (2 mm diameter, rotation 3500 rpm). Scan rate: 15 mV s^{-1}. a) [TBABr] = 0; b) [TBABr] = 0.02 M; c) [TBABr] = 0.075 M. (Plateau currents decrease with the dilution due to additions of TBABr). Inset: variation of R_1 and R_2 half-wave potentials with the co-logarithm of [TBABr].

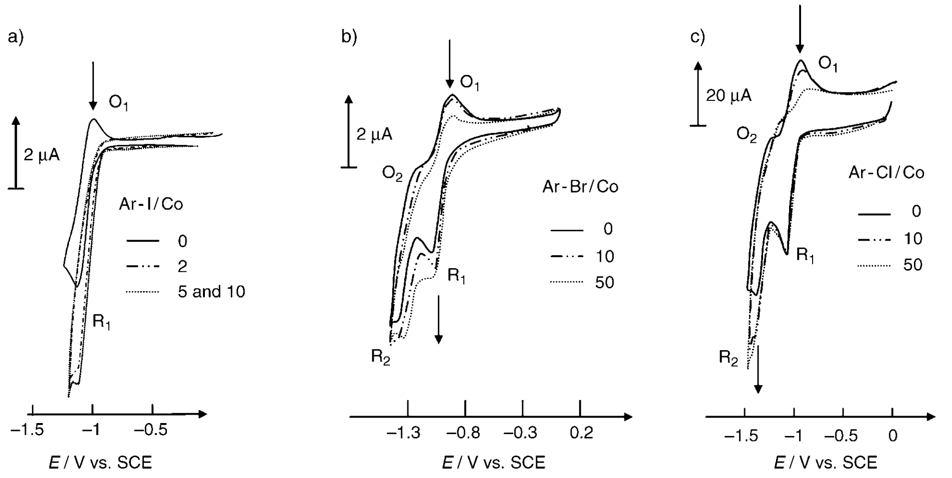


Figure 4. Cyclic voltammograms of $CoBr_2bpy$ 0.005 M in acetonitrile containing 0.1 M $TBABF_4$ in the presence of increasing amounts of a) ethyl 4-iodobenzoate, b) ethyl 4-bromobenzoate and c) methyl 4-chlorobenzoate. electrode: Pt (diameter :0.5 mm (a and b) and 2 mm (c)). Scan rate: 0.2 V s^{-1}. Molar Ar-X/Co ratios are displayed for each series of voltammogram.

though both halides are introduced at the same concentrations, the voltammograms are not affected in the same manner: By introducing increasing amounts of ethyl 4-bromobenzoate, the peak current of wave R_1 increases while the peak current of wave O_1 decreases. In the presence of methyl 4-chlorobenzoate, the raise of intensity is observed at R_2, while the currents at O_1 and O_2 decrease.

The electrochemical behaviour observed in Figure 4a and b is typical of an ECE mechanism where cobalt(I) electrogenerated in peak R_1 reacts with the aromatic iodide or bromide to generate an intermediate species which is also reduced at R_1. In the presence of the most reactive substrate ethyl 4-iodobenzoate (Figure 4a), the peak current at wave R_1 reaches a maximum of about twice its initial value, whatever the excess added. This behaviour precludes a classical redox catalytic process which would give rise to a continuous (catalytic) increase of the peak current at R_1 with increasing amounts of the aromatic iodide. Moreover, the reductions of ethyl 4-iodobenzoate and ethyl 4-bromobenzoate are observed at −1.95 and −2.28 V/SCE, respectively in acetonitrile in our conditions. Such values are too negative with respect to the reduction potential of peak R_1 to further consider the occurrence of a redox catalysis of ArX reduction at R_1. In Figure 4b, the peak current observed at R_2 remains unchanged along ArBr additions (although a slight passivation is observed at 50 molar equivalents of ArBr added). A similar sequence has been reported by us concerning the reactions between aromatic halides and cobalt(I)/pyridine[11] and cobalt(I)/allyl acetate[22] complexes. In both cases, the chemical reaction was an oxidative addition of electrogenerated Co^I on the C–X bond of the aromatic halide, leading to Ar-Co^{III}-XBr which is reduced at the same potential in Ar-Co^{II}-X. The same features are observed in the present work, suggesting the occurrence of an oxidative addition. Indeed, the loss of intensity at O_1 could result from such a reaction, whereas the increase of current intensity at peak R_1 could result from the consecutive reduction of the intermediate Ar-Co^{III}-XBr complex. Since similar phenomena are observed for peak R_2 in the presence of the aromatic chloride, it is likely to assume a comparable cobalt(0) centered ECE sequence involving the oxidative addition of electrogenerated Co^0 on Ar-Cl and the consecutive reduction of the resulting Ar-Co^{II}-Cl into Ar-Co^I. In order to bring further evidences on that issue, we have undertaken to determine the oxidative addition rate constants by plotting the parameter $I_{O_1}^{ArX}/I_{O_1}^{0}$ (representing the reversibility of the system reduced in peak R_1 as a function of a kinetic parameter [ArX]/v representing the competition between ArX concentration and time). Considering that bromide ions are exchanged in the reduction processes observed at R_1 and R_2, the rate constants most likely depend on halide concentration (which varies along ArX conversion). In that context, the constants calculated hereafter are *apparent* rate constants. A representative plot is displayed in Figure 5 for ethyl 4-bromobenzoate.

A particular value of the reversibility of wave R_1 is obtained for $R=0.5$, which corresponds to the half-life of Co^I. Thus, the pseudo-first order oxidative addition rate constant k_1 can be determined,[23] considering that $t_{1/2} = \ln 2/k_1$ for a first order reaction, and that $t_{1/2}$ is estimated from the expresion $t_{1/2} = \{(E_p^{O1}-E^{inv}) + (E_p^{R1}-E^{inv})\}/v$ (E_p^{inv} is the cathodic inversion potential). The intrinsic rate constant k is obtained from $k = k_1/[ArBr]$ and averaged from several couple of values of [ArX] and v which give a reversibility of 0.5. The values of k obtained for various aromatic halides are presented in Table 1.

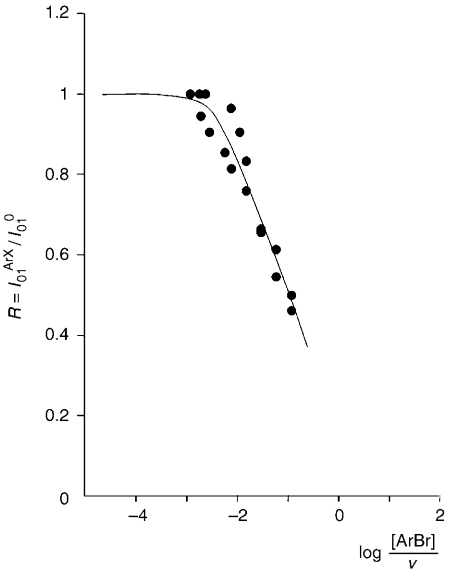


Figure 5. Plot of the reversibility of the system reduced in peak R_1 ($R = I_{O_1}^{ArX}/I_{O_1}^{0}$) as a function of the logarithm of the [ArBr]/v ratio. [ArBr] = concentration of ethyl 4-bromobenzoate: range 0.005 to 0.5 mol dm^{-3}; v = scan rate: range 0.05 to 20 V s^{-1}.

Table 1. Oxidative addition *apparent* rate constants[a] in acetonitrile at 293 K of Co^IBrbpy electrogenerated at R_1 on *para*-substituted aromatic halides.

Entry	1	2	3	4
ArX	I-Ph-CO_2Et	Br-Ph-CO_2Et	Br-Ph-OMe	Cl-Ph-CO_2Me
K	250 ± 30	20 ± 5	3 ± 0.5	1 ± 0.5

[a] All constants in dm^3 mol^{-1} s^{-1}.

As expected, the apparent rate constants decrease in the order I > Br > Cl (Table 1, entries 1, 2 and 4), that is, with the strength of the carbon–halogen bond. Besides, the electronic effect of the substituent in the *para* position dramatically affects the rate constant (Table 1, entries 2 and 3), an electron withdrawing group weakening the C–Br bond. All these results are in agreement with the occurrence of an oxidative addition of Co^I on the aromatic halides.

The shape of the voltammograms in Figure 4c precludes the accurate determination of oxidative addition rate constants of Co^0–bpy electrogenerated in the reduction peak R_2 with aromatic chlorides, at least from the plots depicted in Figure 5. Indeed, the reversibility of the system reduced in peak R_2 is difficult to measure to carry out a similar study as for the system reduced in peak R_1. However, the increase of the intensity in peak current of R_2 is about ten times higher than the one observed at R_1 for the same concentration of methyl 4-chlorobenzoate. Considering that the intensity increases proportionally to the rate constant of the chemical step in an ECE mechanism (electron transfers not rate determining on the plateau of the waves), and by comparison of the currents at R_2 (Figure 4c) with the calculations made at R_1 (Figure 4b) with aryl bromides exhibiting a comparable current increase, the oxidative addition rate constant of Co^0bpy on methyl 4-chlorobenzoate can be roughly estimated to range within $5 < k < 15$ dm^3 mol^{-1} s^{-1}. Thus, Co^0bpy exhibits a higher reactivity than Co^IBrbpy towards aromatic chlorides, and could be the key species in the activation of aromatic chlorides.

Electrochemical behaviour of $CoBr_2$bpy in the presence of isopropenyl acetate: The cyclic voltammograms of $CoBr_2$bpy in the presence of various amounts of isopropenyl acetate (Y) are presented in Figure 6. The presence of the vinylic acetate has a very moderate effect on waves R_1 and O_1, which exhibit thinner shapes, as well as a slight increase of the intensity of R_1. These modifications could be ascribed to a complexation of Co^I by the vinylic acetate, as already observed with cobalt/pyridine complexes.[11] The slight increase

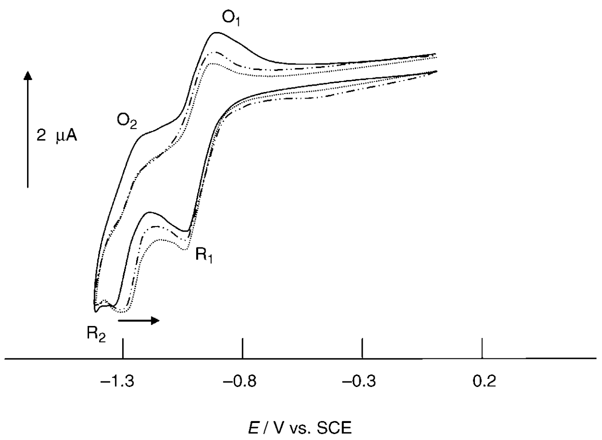


Figure 6. Cyclic voltammograms of $CoBr_2bpy$ 0.005 M in acetonitrile containing 0.1 M $TBABF_4$ in the presence of increasing amounts of isopropenyl acetate (depicted as Y). Electrode: Pt (diameter :0.5 mm). Scan rate: 0.2 V s^{-1}. Molar Y/Co ratios: 0 (——), 5 (–•–•) and 10 (•••••).

of the current at R_1 (associated to a comparable decrease of the current at O_1) could result from an ECE sequence involving the insertion of electrogenerated Co^I in the C–O (vinyl) bond of isopropenyl acetate, as already observed with allylic acetates.[10]

Indeed, the electrolysis of a solution containing $CoBr_2bpy$ and an excess of isopropenyl acetate, carried out in a two-compartment cell on the plateau of wave R_1 allows the consumption of Y. A similar behaviour has been observed from cobalt/pyridine complexes and allyl acetate,[10] which led to the formation of both 1,5-hexadiene (dimer) and propene (hydrogenation product), together with the release of inactive $Co^{II}(OAc)_x$. Although we have not characterized the volatile products formed (isopropene and/or 2,3-dimethylbutadiene), C–O(vinyl) bond cleavage is observed with electrogenerated Co^IBrbpy, and that reaction proceeds rather slowly according to the moderate changes at R_1.

The modifications appear more dramatic on the level of wave R_2, which shifts towards more positive potentials with increasing excesses of Y, while its intensity remains unchanged. Therefore, a complexation reaction of Co^0bpy formed at wave R_2 with isopropenyl acetate is most likely observed. Unfortunately, passivation of the platinum electrode was observed at low scan rates in the presence of isopropenyl acetate, which prevented us from performing stationary voltammetry and analyze how the half wave potential at R_2 varied with the concentration of Y. However, the peak potential of R_2 exhibits a variation of 40 to 65 mV per decade of concentration, which is in keeping with a complexation of Co^0 by Y.

Effect of the simultaneous presence of aromatic halides and isopropenyl acetate: We have established in the latter paragraph that isopropenyl acetate acts both as a Co^0-stabilizing agent and as a potential substrate with a reactive C–O (vinyl) bond. Likewise, aromatic halides undergo oxidative addition with either Co^I- or Co^0–bipyridine complexes electrogenerated at R_1 or R_2, respectively. One can wonder how these reactions are sequenced, that is, which one succeeds to the other in the reaction path leading to the coupling of the aryl and vinyl moieties. That point has been qualitatively studied by cyclic voltammetry, from $CoBr_2bpy$ solutions containing an excess of both substrates. In the case of an activated aromatic bromide (ethyl 4-bromobenzoate), the voltammograms presented in Figure 4b do not exhibit significant changes in the R_1/O_1 region if recorded in the absence or presence of isopropenyl acetate. Indeed, the ECE sequence at R_1 is still observed. Thus, the assumption that we made about the very moderate stabilizing effect of isopropenyl acetate on Co^I is confirmed, since its reactivity towards aromatic bromides is not affected. Conversely, the voltammograms presented in Figure 7 with methyl 4-chlorobenzoate show that the cobalt(0)-centered ECE scheme at R_2 is "frozen" in the presence of isopropenyl acetate.

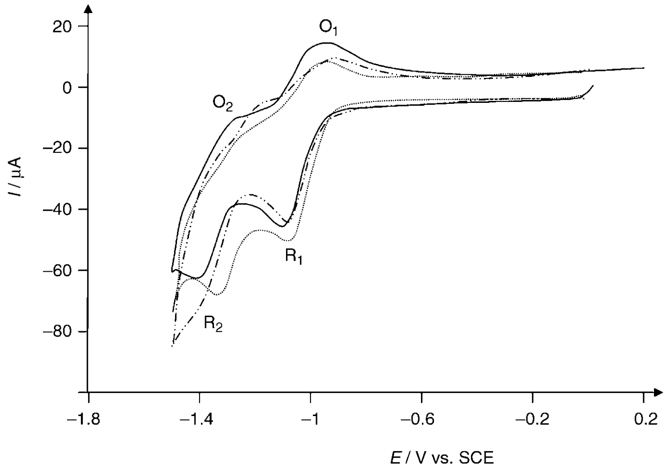


Figure 7. Cyclic voltammograms of $CoBr_2bpy$ 0.005 M in acetonitrile containing 0.1 M $TBABF_4$. Electrode: Pt (diameter :2 mm). Scan rate: 0.2 V s^{-1}. a) No additive (——). b) In the presence of 0.1 M methyl 4-chlorobenzoate (Ar-Cl) (–•–•). c) In the presence of both 0.1 M methyl 4-chlorobenzoate and 0.1 M isopropenyl acetate (Y) (•••••).

Indeed, the increase in current intensity on peak R_2 in the presence of Ar–Cl that came from the consecutive reduction of the Ar-Co^{II}-X intermediate is no longer observed. Since electron transfers are not rate-determining, such a quenching results from a much slower chemical reaction, that is, a slower oxidative addition between Co^0 electrogenerated at R_2 and Ar–Cl. With excess amounts of Y, the decrease of the rate of the oxidative addition is therefore ascribed to a decrease of the concentration of Co^0, which is engaged in the above mentioned complexation reaction with isopropenyl acetate. So, the complexation of Co^0 by Y appears to proceed competitively towards oxidative addition on Ar–Cl. This behaviour is akin to the one depicted between Co^I/pyridine complexes, allylic acetates and aromatic halides.[22]

Preparative electrolyses: We have carried out preparative scale electrolyses of acetonitrile solutions containing both the aromatic halide and vinylOAc at potentials corresponding to the plateaus of either R_1 or R_2 waves and monitored the concentrations of the substrates and products as a function of the charge passed. The corresponding plots are represented in Figure 8.

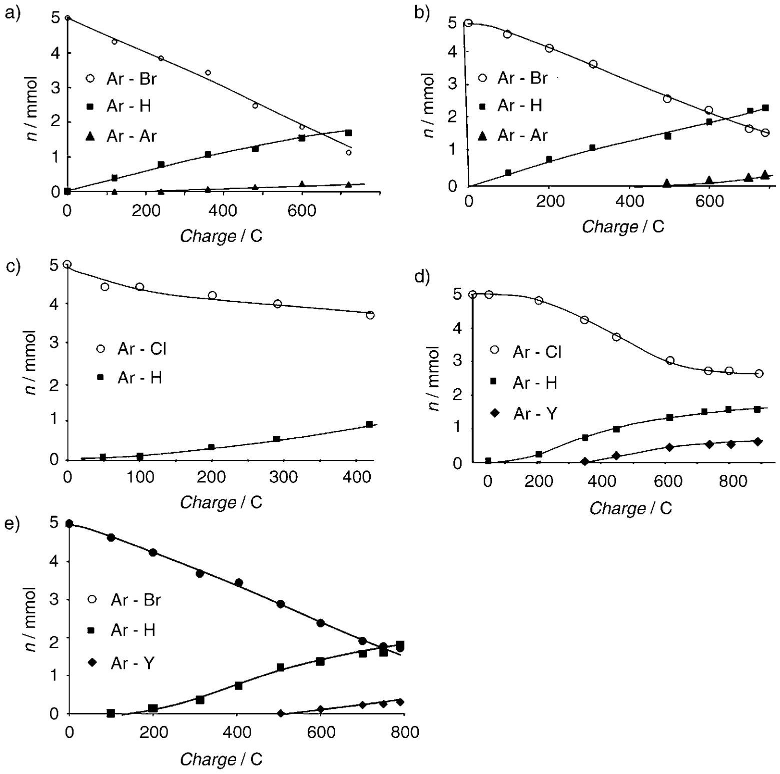


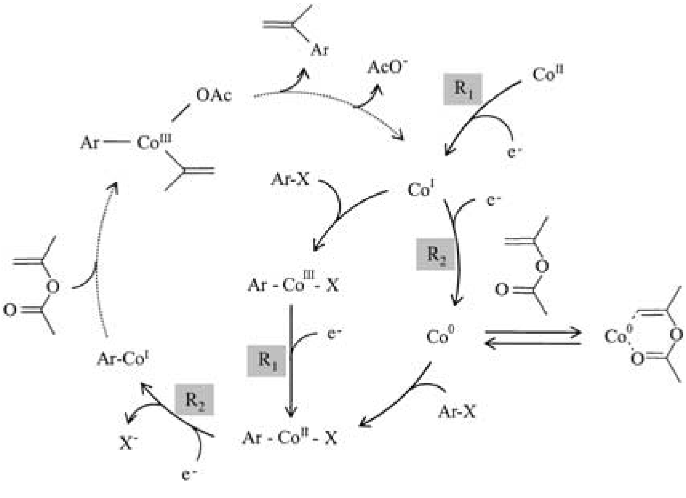
Figure 8. Controlled potential electrolyses of acetonitrile solutions (undivided cell, aluminium sacrificial anode, gold cathode, $TBABF_4$ 0.05 M) containing 0.5 mmol $CoBr_2bpy$ and the following substrates: a) ethyl-4-bromobenzoate (5 mmol), $E=-1.2$ V; b) ethyl-4-bromobenzoate (5 mmol) + isopropenyl acetate (5 mmol), $E=-1.2$ V; c) methyl-4-chlorobenzoate (5 mmol) + isopropenyl acetate (5 mmol), $E=-1.2$ V; d) methyl-4-chlorobenzoate (5 mmol) + isopropenyl acetate (5 mmol), $E=-1.4$ V; e) ethyl-4-bromobenzoate (5 mmol) + isopropenyl acetate (5 mmol), $E=-1.4$ V; Ar-Y= d) 4-isopropenylbenzoic methyl ester or e) 4-isopropenylbenzoic ethyl ester.

As observed from the series of electrolyses reported in Figure 8, the aromatic bromide ArBr is consumed at −1.2 V, and converted into ArH and Ar-Ar in the absence of isopropenyl acetate Y (plot A). In the presence of both ArBr and Y species (plot B), the product distribution is not significantly affected. The aromatic chloride Ar-Cl is also reduced at −1.2 V into ArH with a lower rate, whereas the coupling product Ar-Y is still undetected (plot C). In fact, Ar-Y is formed only when the potential is set at −1.4 V (plots D and E), which is a value corresponding to the plateau of wave R_2. As already discussed in our previous papers,[8,9,11,22] ArH most likely arises from the decomposition of intermediate arylcobalt species in a radical $Ar^{\bullet}$, which abstracts an hydrogen atom from the solvent. The mechanism of the formation of Ar-Ar is not yet elucidated, and the Ar-Ar/Ar-H ratio strongly depends on the conditions (ligand, solvent, potential applied).

These results bring to light a very important aspect of the mechanism involved in the cobalt-catalyzed vinylation of aromatic halides. Indeed, one could expect that aryl chlorides might be harder to reduce than their bromide analogues. In that context, the reduction of $CoBr_2bpy$ at R_2 into Co^0 would allow the activation of the C−Cl bond. However, since aromatic chlorides are consumed at R_1 and Ar-Y formed only at R_2, the activation of the C−Cl bond—although more efficient at R_2—does not appear to be the determining step in the overall coupling reaction. So, the key species reduced at −1.4 V is most likely an intermediate arylcobalt complex. Owing to the electrochemical reduction/oxidative addition/reduction (ECE) sequences brought out in the first part of this work, the complex formed at R_2, depicted as $Ar\text{-}Co^{I}$ would be the reactive species toward the vinylic acetate. In that context, an intermediate arylvinylcobalt(III) species would be formed, releasing the coupling product and Co^{I} according to a reductive elimination. We have no electrochemical means to characterize and discriminate the regeneration of a determined Co^{II} or Co^{I} complex (as far as the chemical steps proceed fast enough) since both complexes are reduced at −1.4 V. Hence, the ultimate steps of the coupling process remain hypothetical. The catalytic cycle represented in Scheme 1 summarizes the experimental results (note that the uncharacterized steps are represented by dashed lines).

Conclusion

The electrochemical behaviour of $CoBr_2bpy$ has revealed the possibility to generate both soluble Co^{I} and Co^0 complexes in acetonitrile, the latter being stable over few seconds (time scale of our CV experiments). Such Co^0–bipyridine complexes are not obtained from $[Co(bpy)_3]^{2+}$ precursors which are generally used for electroanalytical/mechanistic studies. We have established that the electrogenerated Co^0 complex allows the activation of the strong C−Cl bond of aromatic chlorides according to an oxidative addition which proceeds faster than the one obtained from electro-



Scheme 1.

generated Co^I. That raise in reactivity (compared with the more stable low-valent cobalt complexes) is of great synthetic interest, since the range of aromatic halides which can be used in organic preparative chemistry is dramatically enhanced. Isopropenyl acetate (used as a model of vinylic acetate) appears to act as a stabilizing complexing agent toward electrogenerated Co^0. The electrochemical behaviour of $CoBr_2bpy$ in the presence of both the aromatic halide and isopropenyl acetate has showed that complexation is competitive (therefore not preceding) toward the oxidative addition of Co^0 on the aromatic halide. The preparative electrolyses have raised up a second important point, which is the necessity to set the reduction potential at a value as negative as −1.4 V to achieve the coupling between the aryl and allyl moieties. This behaviour has led us to assume the occurrence of an additional reduction step of an arylcobalt(II) complex leading to an arylcobalt(I) intermediate, which would undergo oxidative addition on the vinylic acetate. These results are consistent with a cobalt(I)-centered catalytic scheme. Unexpectedly, the activation of stable aromatic chlorides is not the limiting step of the process, which requires relatively strong electrochemical or chemical reducing conditions. Many points remain to be explored, namely the factors which affect the stability and reactivity of the intermediate arylcobalt species, such as the nature and concentration of the halide ions which are associated to the cobalt center, the nature of the solvent. However, $CoBr_2bpy$ appears to be a very interesting catalytic precursor exhibiting both an excellent reactivity toward aromatic halides and a good stability.

Experimental Section

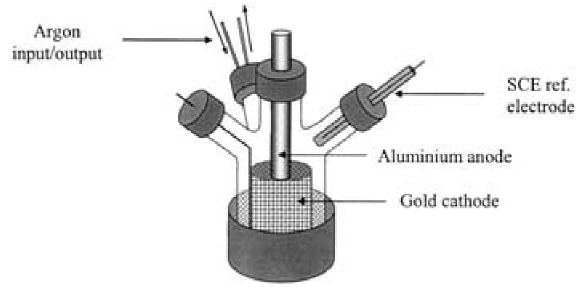
Reagents: Acetonitrile was purchased from SDS (analytical grade), stored under argon atmosphere, and used without further purification.

Substrates (aryl bromides, isopropenyl acetate) were purchased from Acros and Aldrich Chemicals and used as received.

Tetrabutylammonium tetrafluoroborate was purchased from Fluka and recrystallised from diethyl ether.

$CoBr_2bpy$ catalyst precursor was prepared in ethanol from stoichiometric amounts of $CoBr_2$ and 2,2′-bipyridine (both compounds purchased from Aldrich). After overnight stirring, the grey precipitate obtained was filtered, washed with ethanol and dried for 12 h at 50 °C under vacuum. Elemental analysis: C (36.06 %), Br (36.98 %). The same complex could be formed in situ in acetonitrile by introducing stoichiometric amounts of $CoBr_2$ and 2,2′-bipyridine. The acetonitrile solutions of $CoBr_2bpy$ are pale-green. Note that $CoBr_2bpy$ exhibits a moderate solubility in acetonitrile at room temperature (precipitation observed beyond $0.015\ mol\,dm^{-3}$).

Procedures of electrolyses and product identification: The preparative electrolyses (controlled potential, at −1.2 V -R_1- or −1.4 V -R_2-) of acetonitrile solutions ($50\ cm^3$) containing a catalytic amount (0.5 mmol, that is, 10 mol %) of $CoBr_2bpy$ and stoichiometric amounts (5 mmol) of aromatic halides (Ar-X) and/or isopropenyl acetate (Y) are performed in an undivided batch cell fitted with a sacrificial cylindrical aluminium anode which is surrounded by a gold grid cathode, as schematized below.



The concentration of the substrates was monitored by GC using an internal standard (dodecane) from aliquots of the solutions which were hydrolyzed with 0.1 M aqueous HCl and extracted in diethyl ether. The identification of substances formed during the electrolyses (Ar-X, Ar-H, Ar-Ar, Ar-Y) was achieved by GC/MS. Volatile isopropenyl acetate (Y), as well as its cleavage product (isopropene) are not separated from diethyl ether under our GC conditions, and therefore not quantified.

Apparatus: Electrolyses and voltammetry were performed using an EG&G-PARC 273 A potentiostat together with M270 electrochemical software. All potentials are referred to a saturated calomel electrode (SCE).

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Received: September 22, 2004
Revised: March 15, 2005