Stabilization of Co^I by Zn^{II} in Pure Acetonitrile and its Reaction with Aryl Halides

Sylvaine Seka, Olivier Buriez,* and Jacques Périchon[a]

Abstract: The study of the electrochemical behavior of cobalt(II) bromide ($CoBr_2$) in pure acetonitrile allowed us to demonstrate that Co^{2+} is the catalyst precursor involved in the electrochemical and chemical conversions of arylhalides, ArX, to arylzinc compounds in that solvent. The reduction of Co^{2+} leads to the Co^+ species, which disproportionates too rapidly to react further with aryl halides. However, the presence of zinc(II) bromide allows us to stabilize the electrogenerated cobalt(I) and to observe it on the timescale of slow cyclic voltammetry. Under such conditions, the Co^I species has time to react with aryl halides and produce $[Co^{III}ArX]^+$ complexes that are reduced into $[Co^{II}ArX]$ by a single electron uptake at the same potential at which Co^{2+} is reduced. Rate constants for the oxidative addition of ArX to Co^I have been determined for various aryl halides and compared to the values obtained in an acetonitrile (ACN)/pyridine (9:1, *v*/*v*) mixture. It is shown that Co^I is stabilized more by $ZnBr_2$ than by pyridine. A transmetallation reaction between $[Co^{II}ArX]$ and $ZnBr_2$ has also been observed. We finally propose a mechanism for the cobalt-catalyzed electrochemical conversion of aryl bromides into organozinc species in pure acetonitrile.

Keywords: aryl halides · cobalt · electrochemistry · kinetics · zinc bromide

Introduction

The preparation of organozinc compounds, which are key intermediates in the selective synthesis of carbon–carbon bonds from highly functionalized substrates,[1] has been the subject of increased interest over the last decade.

The preparation of such compounds was formerly achieved by the preliminary formation of aryllithium reagents followed by transmetallation with zinc halides. Nevertheless, this method is not easily achieved with aryl compounds bearing reactive functional groups such as ketones, nitriles or esters, since very low reaction temperatures are required.[2] This drawback can be overcome with the use of activated zinc (Rieke's zinc) obtained by reduction of zinc halide with alkali metal naphthalenide. However, the difficulty of handling this reagent makes this method very sensitive.[3, 4]

As an alternative to these chemical procedures, we have successfully synthesized arylzinc compounds in high yields and under mild conditions by two electrochemical procedures. The former one involves nickel complexes as catalysts in dimethylformamide (DMF) as solvent.[5] Recently, we have developed a simpler electrocatalytic system using cobalt salts (CoX_2, X = Br, Cl) as catalysts.[6] Indeed, reactions can be conducted in acetonitrile (ACN) or DMF associated to pyridine, and a less toxic catalyst is used. We have also developed a pyridine-free process for the electrochemical preparation of arylzinc compounds in pure acetonitrile that allows coupling reactions with electrophiles.[7]

These electrochemical methods, which use very simple experimental conditions in comparison with known chemical processes, enable the formation of arylzinc compounds in high yields, and the process applies notably to aryl halides bearing electron-withdrawing group.

More importantly, on the base on our recent discoveries we have found a new and facile chemical synthesis of functionalized arylzinc species from aromatic or thienyl bromides, always under mild conditions and in pure acetonitrile, by using a simple cobalt catalyst and zinc dust.[8] This last process can be easily extended to larger scale.

Surprisingly, the last two methods (chemical and electrochemical) discovered in our group for the preparation of organozinc compounds have been carried out in the absence of pyridine, which was required in our former processes to stabilize the cobalt(I) catalyst. Consequently, these new results prompted us to investigate the electrochemical behavior of $CoBr_2$ both in the absence and the presence of aryl halides and zinc bromide in pure acetonitrile in order to elucidate the involved mechanisms. This important work is required to improve our reactions and to discover other useful syntheses.

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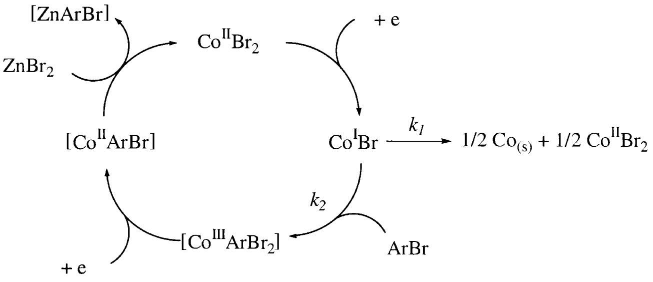
The electrochemical behavior of $CoBr_2$ has already been examined in ACN/pyridine and DMF/pyridine (9:1) mixtures.[9, 10] Results obtained in both solvents are similar and can be summarized as follows: the reduction of $CoBr_2$ leads to a cobalt(I) species that is stable on the timescale of cyclic voltammetry (few tenths of a millisecond). However, it is not as stable as those obtained by reduction of cobalt(II) in the presence of salen, vitamin B_{12}, or bipyridine as ligands.[11–24] Indeed, on the timescale of slow cyclic voltammetry or electrolysis it undergoes a disproportionation reaction leading to solid cobalt and half of the starting cobalt(II). The rate constant k_1 for this reaction has been found equal to $(1 \pm 0.25) \times 10^3\,\text{M}^{-1}\text{s}^{-1}$ in ACN/pyridine.[10] We also showed that the electrogenerated Co^I reacts with aryl halides, ArX, leading to arylcobalt(III) complexes that are reduced into arylcobalt(II) species at the same potential as $CoBr_2$. The rate constant k_2 for this oxidative addition depends on both the nature of the halogen and the substituent on the aromatic ring. The values obtained for k_2 have been found in the range $30-2600\,\text{M}^{-1}\text{s}^{-1}$ in ACN/pyridine.[10] Thus, a competition exists between the disproportionation reaction (k_1) and the oxidative addition (k_2) (Scheme 1). Furthermore, we detected a transmetallation reaction between arylcobalt(II) complexes and zinc(II) bromide that leads to the arylzinc compound and regenerates the cobalt(II) catalyst. This allowed us to fully elucidate the mechanism for the electroformation of arylzinc compounds in DMF or ACN/pyridine (Scheme 1).[25] We have also demonstrated in DMF/pyridine the stabilization of the electrogenerated Co^I species by the presence of zinc bromide, but this has no effect on the oxidative addition rate constant of ArX to Co^I relative to results obtained in the absence of $ZnBr_2$.



Scheme 1. Mechanism for the electrochemical conversion of aryl halides to arylzinc species in DMF or ACN/pyridine (9:1) in the presence of zinc bromide and with cobalt bromide as catalyst. All the cobalt species are supposed to be coordinated by a pyridine ligand, which has been omitted for simplification.

In the present work we have examined the electrochemical behavior of $CoBr_2$ in pure acetonitrile both in the absence and the presence of aryl halides and zinc(II). We especially establish that Co^{2+} is the real cobalt(II) catalyst precursor involved in the electrochemical and chemical conversions of aryl halides into arylzinc compounds in pure acetonitrile and that the stabilization of Co^+ by a halogenated zinc(II) species is the key step in such processes.

Results and Discussion

Study of the electrochemical behavior of $CoBr_2$ in pure acetonitrile—evidence for the reduction of Co^{2+}: The cyclic voltammogram obtained by reduction of $CoBr_2$ in pure acetonitrile at a platinum disk electrode and at a scan rate $v = 0.2\,\text{V}\,\text{s}^{-1}$ exhibits an irreversible reduction wave R_1 at $E_{R1} = -0.86$ V versus SCE (saturated calomel electrode). Under the same conditions (concentration, scan rate, electrode, etc.) the reduction current of R_1 is smaller than that obtained in an acetonitrile (ACN)/pyridine (9:1, *v/v*) mixture. The backward potential scan reveals an ill-defined oxidation wave O_2 corresponding to the oxidation of solid cobalt deposited at the electrode surface, and coming from the disproportionation reaction of the Co^I species electrogenerated at R_1 (Figure 1).[10] A study of R_1 as a function of the scan rate shows the absence of reversibility until $200\,\text{V}\,\text{s}^{-1}$, whereas it was reversible from a few volts per second in ACN/pyridine (9:1). Therefore, the disproportionation reaction of the electrogenerated Co^I species is much faster in pure acetonitrile than in ACN/pyridine (9:1), in agreement with the stabilization of Co^I by pyridine.[10]

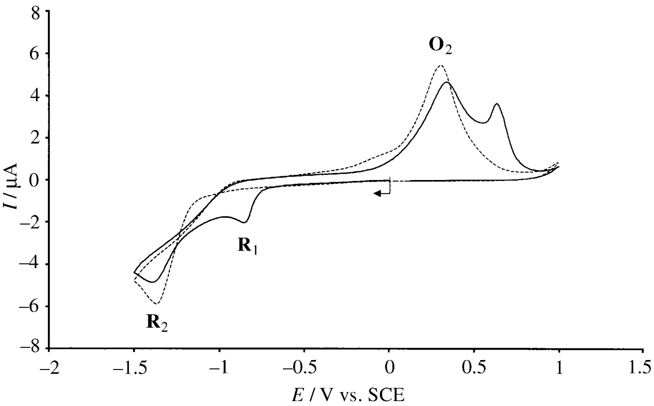


Figure 1. Cyclic voltammograms of $CoBr_2$ (5 mM) in acetonitrile + NBu_4BF_4 (0.1 M) recorded at a platinum disk electrode (0.5 mm diameter) at $v = 0.2\,\text{V}\,\text{s}^{-1}$ and at RT. Complex alone (——) and in the presence of one molar equivalent of $n\text{Bu}_4\text{NBr}$ (----).

At more negative potentials, a second reduction wave R_2 was located at $E_{R2} = -1.4$ V. When the voltammogram is run in the presence of one molar equivalent of $n\text{Bu}_4\text{NBr}$, R_1 is no longer detected, whereas the reduction current of R_2 increases slightly (Figure 1). In the presence of more than one equivalent of $n\text{Bu}_4\text{NBr}$, R_2 shifts towards more negative potential values. These results demonstrate the existence of a chemical equilibrium between the cobalt(II) species and bromide ions, and are in agreement with already reported studies showing that $CoBr_2$ is an equilibrium mixture of the $[CoBr]^+$, $[CoBr_2]$, $[CoBr_3]^-$, $[CoBr_4]^{2-}$, and Co^{2+} species in pure acetonitrile.[26] Among these species the last one should be most readily reducible. To verify this point, we recorded the cyclic voltammogram of an authentic solution of Co^{2+} (15 mM) prepared from the oxidation of a cobalt rod (see Experimental Section). As shown in Figure 2, the Co^{2+} species is reduced in a single wave at -0.86 V and at $v = 0.2\,\text{V}\,\text{s}^{-1}$ in

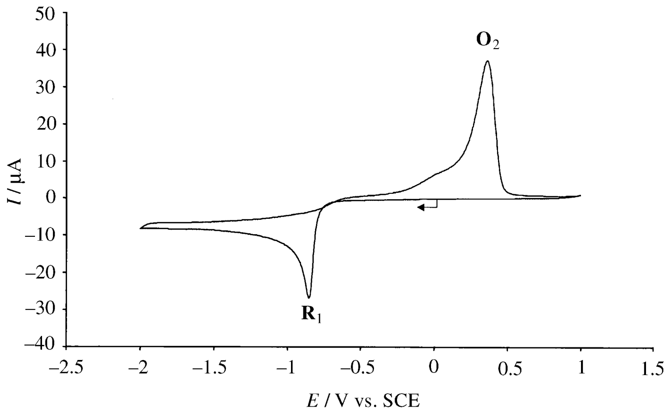


Figure 2. Cyclic voltammogram of Co^{2+} (15 mM) in acetonitrile + NBu_4BF_4 (0.1 M) recorded at a platinum disk electrode (0.5 mm diameter) at $v = 0.2\ V\,s^{-1}$ and at RT.

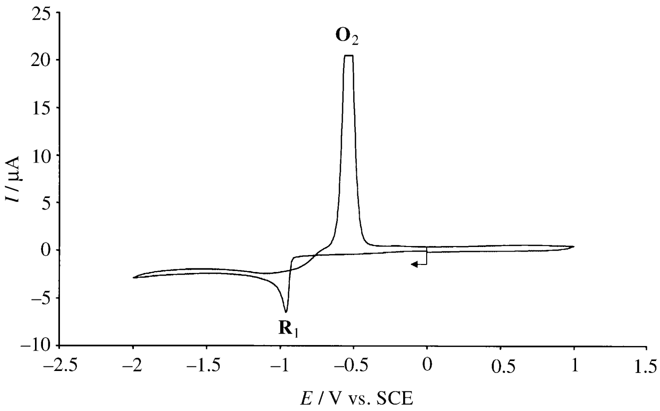


Figure 3. Cyclic voltammogram of Zn^{2+} (5 mM) in acetonitrile + NBu_4BF_4 (0.1 M) recorded at a platinum disk electrode (0.5 mm diameter) at $v = 0.2\ V\,s^{-1}$ and at RT.

pure acetonitrile. This result clearly establishes that R_1, observed in Figure 1, corresponds to the reduction of Co^{2+} to Co^+, whereas R_2 is likely to correspond to the reduction of a brominated cobalt(II) species [Eqs. (1) and (2)].

$$Co^{2+} + e \rightarrow Co^+ \quad (1)$$

$$Co^+ \xrightarrow{k_{disp}} \tfrac{1}{2}Co^{2+} + \tfrac{1}{2}Co_{(s)} \quad (2)$$

Comparison of reduction currents of R_1 obtained from known concentrations of Co^{2+} and $CoBr_2$ under the same conditions (scan rate, electrode, etc.), indicates that about 30% of $CoBr_2$ leads to the Co^{2+} species when dissolved in pure acetonitrile.

Interestingly, the cyclic voltammogram obtained for a solution of Co^{2+} (5 mM) in the presence of excess ethyl 4-bromobenzoate was not modified and, especially, the intensity of O_2 did not decrease; this indicates that no reaction between Co^I and the aryl bromide takes place, because of a too fast disproportionation reaction of the electrogenerated cobalt(I) species. By comparison, the rate constant for the reaction between Co^I and ethyl 4-bromobenzoate obtained in ACN/pyridine (9:1) had been found equal to $(2.25 \pm 0.35) \times 10^3\ M^{-1}s^{-1}$, whereas the disproportionation rate constant of Co^I was equal to $(1 \pm 0.25) \times 10^3\ M^{-1}s^{-1}$.[10]

However, the electrochemical and chemical conversions of aryl bromides to arylzinc compounds by cobalt catalysis are possible in pure acetonitrile.[5, 8] This prompted us to study the effect of zinc(II) on the electrochemical behavior of Co^{2+}.

Study of the electrochemical behavior of cobalt(II) in the presence of zinc(II) in pure acetonitrile—evidence for the stabilization of the electrogenerated Co^+: As previously shown for $CoBr_2$, it probably exists as an equilibrium mixture of several zinc(II) species when $ZnBr_2$ is dissolved in pure acetonitrile.[27] A cyclic voltammogram of $ZnBr_2$ (5 mM) at $0.2\ V\,s^{-1}$ at a platinum disk electrode exhibits a reduction wave located at $E = -0.96$ V, which actually corresponds to the reduction of Zn^{2+} by comparison with the cyclic voltammogram obtained from an authentic solution of electrogenerated Zn^{2+} (Figure 3). Therefore, Zn^{2+} is reducible at a more negative potential than Co^{2+}.

The addition of increasing amounts of $ZnBr_2$ causes several changes in the cyclic voltammogram of $CoBr_2$ obtained at $0.2\ V\,s^{-1}$ in pure acetonitrile: 1) the intensity of R_1 corresponding to the reduction of Co^{2+} increases, 2) R_1 becomes reversible (wave O_1), and 3) the oxidation current of O_2 decreases. Moreover, the reduction wave of Zn^{2+} is not detected. Intensities of both R_1 and O_1 are at a maximum in the presence of five molar equivalents of $ZnBr_2$ with respect to $CoBr_2$ (Figure 4). The appearance of O_1 and the disappearance of O_2 in the same timescale are in agreement with a stabilization of Co^+ by a zinc(II) species. Moreover, the increase in the reduction current of R_1 cannot be due to the reduction of Zn^{2+}, which occurs at a potential more negative than the reduction of Co^{2+}. Indeed, this would result in an oxidation wave located at $E = -0.65$ V on the cyclic voltammogram corresponding to the oxidation of solid zinc deposited at the electrode surface (Figure 3). As a matter of fact, this phenomenon can be explained by a reaction taking place between both $ZnBr_2$ and $CoBr_2$, and consisting of the transfer of bromide ions from cobalt(II) to zinc(II) as already shown by

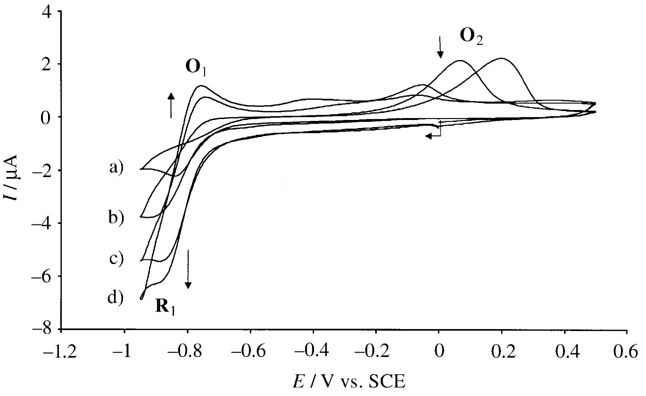


Figure 4. Cyclic voltammograms of $CoBr_2$ (5 mM) in acetonitrile + NBu_4BF_4 (0.1 M) recorded at a platinum disk electrode (0.5 mm diameter) at $v = 0.2\ V\,s^{-1}$ and at RT. a) In the absence of and in the presence of b) one, c) three, and d) five molar equivalents of $ZnBr_2$.

Libus et al. for $CoCl_2$ and $ZnCl_2$ in pure acetonitrile.[28] Therefore, this reaction leads to an increase in the concentration of Co^{2+} and consequently to an increase in the intensity of R_1. In that case, one or several zinc(II) species of the type $(Zn^{II}Br_x)^{(x-2)-}$ would be formed.

As mentioned above, the cyclic voltammogram of Co^{2+} (15 mM), prepared from the oxidation of a cobalt rod, exhibits both an irreversible reduction wave R_1 at -0.86 V and the oxidation of solid cobalt coming from the disproportionation reaction of Co^I (wave O_2). With the addition of one molar equivalent of $ZnBr_2$ the reduction wave R_1 becomes reversible and its intensity is halved. In addition, O_2 disappears on the same timescale (Figure 5).

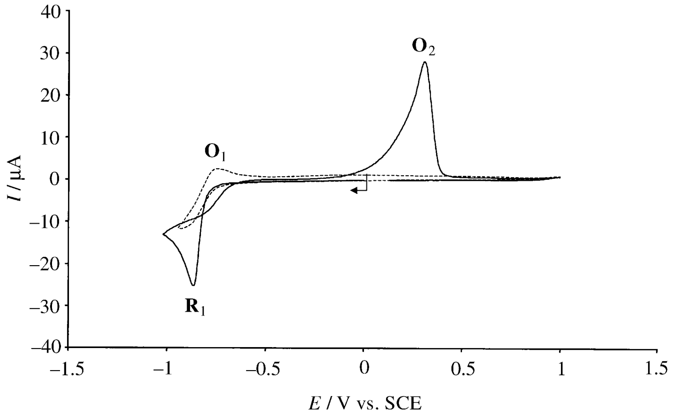


Figure 5. Cyclic voltammograms of Co^{2+} (15 mM) in acetonitrile + NBu_4BF_4 (0.1 M) recorded at a platinum disk electrode (0.5 mm diameter) at $v = 0.2\ V\,s^{-1}$ and at RT. Complexe alone (——) and in the presence of one molar equivalent of $ZnBr_2$ (- - - -).

The use of the method combining chronoamperometry and steady-state voltammetry allowed us to establish that wave R_1 is monoelectronic in the presence of zinc(II) ($n_e = 1.07 \pm 0.23$).[29] This confirms the stabilization of Co^+ by a zinc(II) species and the absence of a disproportionation reaction of the former in the range of a few seconds. The cobalt(I) species is therefore more stable in the presence of $ZnBr_2$ than in the presence of pyridine.

Interestingly, the cyclic voltammogram obtained by reduction of Co^{2+} in the presence of Zn^{2+}, both electrochemically prepared, does not display any reversibility for R_1 and no decrease in the oxidation current of O_2, indicating that the presence of bromide ions is required to stabilize the Co^+ species.

The stabilization of Co^+ by $ZnBr_2$ was then studied in preparative-scale electrolyses leading to organozinc compounds. Experiments were conducted in an undivided electrochemical cell in the presence of PhBr as the aryl halide and at constant current ($I = 0.2$ A) as described in the Experimental Section. The potential value was constant and equal to -0.8 V. Table 1 shows that the presence of increasing amounts of zinc bromide affords a larger consumption of PhBr. This is especially observed above two molar equivalents of $ZnBr_2$ with respect to $CoBr_2$. This result is in agreement with a better stabilization of the electrogenerated Co^+, which leads to an increase in the catalyst turnover and a decrease in the catalyst loss through the disproportionation reaction. As expected, the yield of the arylzinc ([ZnPhBr]) increases with increasing amounts of $ZnBr_2$.

Table 1. Preparative-scale electrolyses. Effect of the zinc bromide amount on the consumption of PhBr in pure acetonitrile. $[CoBr_2] = 23$ mM.

$[ZnBr_2]$ [mM]	PhBr recovered [%]	PhZnBr [%]
0	55	15
46	55	15
69	38	25
92	17	38

In view of the preceding results, it was of interest to know whether Co^+ would be stable in the presence of zinc(II) on the timescale of a preparative electrolysis (range of a few minutes). Accordingly, controlled-potential electrolysis of Co^{2+} (0.5 mmol) in the presence of zinc bromide (0.5 mmol) was carried out at -0.75 V. The electrolysis was stopped after a charge of one electron per mole of Co^{2+} was passed in order to generate the corresponding Co^+ stabilized by a zinc(II) species. This was then added to a solution containing ethyl 4-bromobenzoate (1 mmol). Examination of that final mixture as a function of time did not show any consumption of the aryl halide, demonstrating that Co^+ is not sufficiently stable even in the presence of $ZnBr_2$ to react with the halide. Under these conditions, its half-life can be estimated to be a few seconds.

Evidence for a reaction between the stabilized Co^I species and aryl halides (ArX)—kinetic investigations: The reaction between the electrogenerated cobalt(I) species and aryl halides was then examined in the presence of zinc bromide by means of cyclic voltammetry. As previously noticed, the reduction wave of Co^{2+} obtained in the presence of $ZnBr_2$ is reversible and no disproportionation of Co^I occurs. In the presence of aryl halides (ArX) the intensity of the oxidation current of O_1 (oxidation of Co^+ into Co^{2+}) decreases more or less according to the nature of ArX, and R_1 is slightly shifted towards more positive potential value. This indicates a reaction between the electrogenerated Co^+ and ArX that probably leads to the corresponding arylcobalt(III) complex. The efficiency of this reaction can be quantified from the ratio $R = I_{ArX}/I_0$, whereby I_{ArX} and I_0 are the peak current of the oxidation wave O_1 (oxidation of Co^+ produced in R_1) in the presence and absence of ArX, respectively, at the same sweep rate and on the same electrode.[30, 31] A series of voltammograms was recorded for solutions of $CoBr_2$ (5 mM) in the presence of $ZnBr_2$ (15 mM) at scan rates ranging from 0.2 to 30 $V\,s^{-1}$ and at concentrations of ArX from 5 to 1200 mM. For each experiment the ratio R was measured, and the corresponding set of values plotted against $[ArX]/v$ (Figure 6 for 4-bromoanisole).

From a ratio $R = 0.5$, the rate constant for the reaction between Co^I and ArX was determined through the half-life of the Co^I species.[32] Similar results were obtained for Co^{2+} (5 mM) in the presence of one molar equivalent of $ZnBr_2$. Results are summarized in Table 2.

The rate constant (k_2) obtained for the reaction between Co^I and ArX in pure ACN and in the presence of zinc bromide

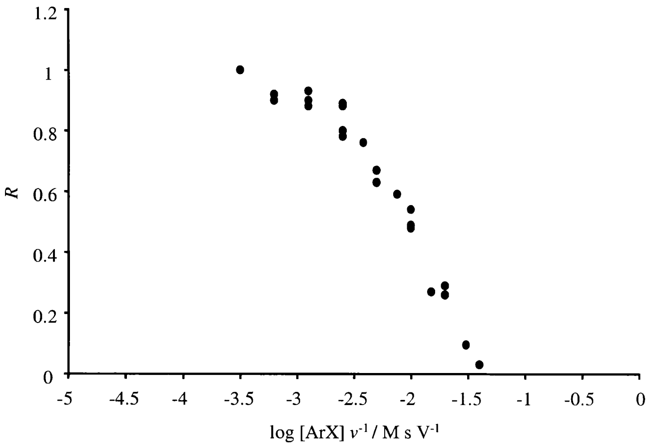
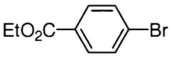
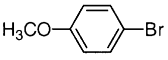
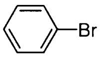
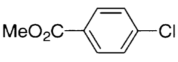
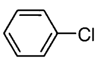


Figure 6. Efficiency of the reaction between Co^+ and 4-bromoanisole (ArX) from the variation of the peak current ratio $R = I_{ArX}/I_0$ as a function of log([ArX]/v), $10 < v < 30\ V s^{-1}$ and $5 < [ArX] < 150\,mM$ in pure acetonitrile + nBu_4NBF_4 (0.1M) and in the presence of three molar equivalents of $ZnBr_2$ with respect to $CoBr_2$ (5mM).

Table 2. Rate constants for the reaction between Co^+ and various aryl halides at room temperature in pure acetonitrile + nBu_4NBF_4 (0.1M) and in the presence of zinc bromide (15mM). $[CoBr_2] = 5\,mM$.

ArX	k_2 [$M^{-1}s^{-1}$]
	430 ± 80
	400 ± 90
	330 ± 80
	2 ± 1
	< 1

show a decrease by a factor of about five, compared with data given in reference [10] for the k_2 values of the same reaction obtained in ACN/pyridine (9:1). This is in agreement with a higher stabilization of Co^I by $ZnBr_2$ than by pyridine. Interestingly, we had already shown in DMF/pyridine (9:1) that $ZnBr_2$ stabilizes the cobalt(I) species, but this had no influence on the oxidative addition rate constant of ArX to Co^I.[25] The presence of pyridine would thus inhibit the zinc effect.

Furthermore, with the addition of aryl halides, the intensity of the peak current of R_1 increases until a maximum value. This increase depends on both the nature and the amount of ArX and the scan rate. It is thus very large for low scan rates in the presence of aryl halides that react very rapidly with Co^I (Figure 7 for ethyl 4-iodobenzoate at $v = 0.2\ V s^{-1}$). This behavior, already described in previous work,[9] indicates that the arylcobalt(III) complex obtained after the reaction between Co^+ and ArX is reduced at the level of R_1 into the corresponding arylcobalt(II) compound [Eqs. (3) and (4)].

$$Co^+ + ArX \rightarrow [Co^{III}ArX]^+ \tag{3}$$

$$[Co^{III}ArX]^+ + e^- \rightarrow [Co^{II}ArX] \tag{4}$$

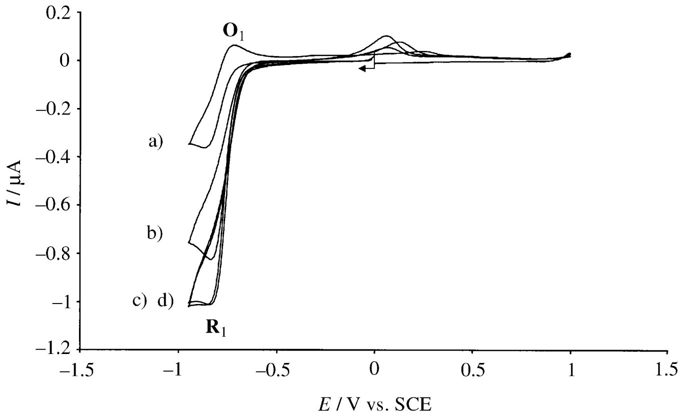


Figure 7. Cyclic voltammograms of Co^{2+} (5mM) in the presence of $ZnBr_2$ (5mM) in acetonitrile + NBu_4BF_4 (0.1M) recorded at a platinum disk electrode (0.125 mm diameter) at $v = 0.2\ V s^{-1}$ and at RT. a) In the absence of and b) in the presence of two, c) six, and d) eight molar equivalents of ethyl 4-iodobenzoate.

Interestingly, if under the conditions described in Figure 7, increasing amounts of $ZnBr_2$ are added to the solution, the peak current of R_1 increases again indicating a catalytic process (Figure 8 in comparison with Figure 7).

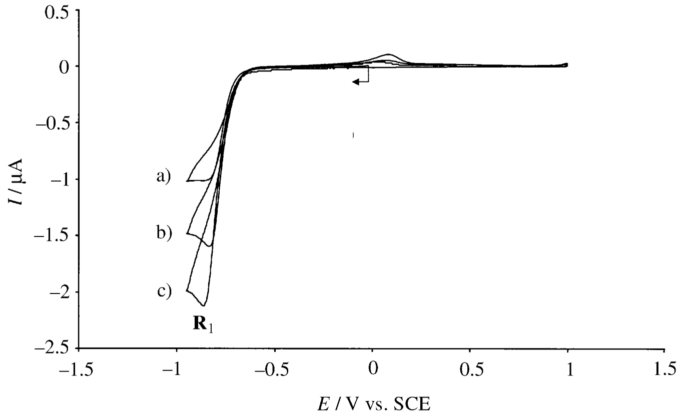
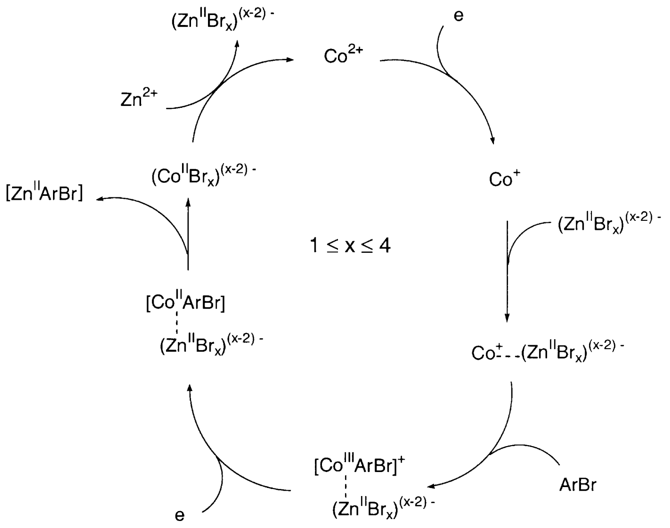


Figure 8. a) Cyclic voltammograms of Co^{2+} (5mM) in the presence of $ZnBr_2$ (5mM) and ethyl 4-iodobenzoate (40mM) in acetonitrile + NBu_4BF_4 (0.1M) recorded at a platinum disk electrode (0.125 mm diameter) at $v = 0.2\ V s^{-1}$ and at RT. Then, in the presence of b) 10 and c) 15 mM of $ZnBr_2$.

The possible reduction of $ZnBr_2$ which occurs at a potential more negative than the reduction of Co^{2+} can be ruled out. Indeed, this would result in an oxidation wave located at $E = -0.65\ V$ on the cyclic voltammogram corresponding to the oxidation of solid zinc deposited at the electrode surface. Therefore, the observed catalytic current can only be due to the regeneration of cobalt(II) following a transmetallation reaction between $[Co^{II}ArBr]$ and zinc(II).

Mechanism of the electrochemical conversion of aryl halides to arylzinc compounds by cobalt catalysis in pure acetonitrile: According to the results previously described, we are able to propose a mechanism for the electrochemical conversion of aryl halides to arylzinc compounds by cobalt catalysis in pure ACN and using the sacrificial zinc anode process (Scheme 2).



Scheme 2. Proposed mechanism for the electrochemical conversion of aryl halides to arylzinc compounds by cobalt catalysis in pure acetonitrile and using the sacrificial zinc anode process.

The cycle is initiated by the reduction of Co^{2+} into Co^{+}, which is stabilized by a zinc(II) species. An oxidative addition then occurs between the aryl halides and Co^{+} affording the trivalent cobalt complex $[Co^{III}ArBr]^{+}$ that is still likely to be coordinated to a halogenated Zn(II) species. This is reduced into $[Co^{II}ArBr]$ by a single-electron uptake at the same potential at which Co^{2+} is reduced. A transmetallation reaction between $[Co^{II}ArBr]$ and the zinc(II) species produces the arylzinc compound and regenerates a halogenated cobalt(II) species. This should progressively poison the catalyst because of the formation of $(Co^{II}Br_x)^{(x-2)-}$ species, which become more and more difficult to reduce as x increases. However, the continuous generation of Zn^{2+} coming from the oxidation of the zinc rod allows one to dehalogenate the cobalt(II) and to restore the cobalt catalyst in its initial form Co^{2+}, making the electrosynthesis of organozinc compound possible at a constant potential of -0.8 V.

Conclusion

This work was devoted to the electrochemical behavior of $CoBr_2$ in pure acetonitrile (ACN) in order to discover why the chemical and electrochemical preparations of organozinc compounds, recently discovered in our group,[7, 8] can be achieved in the absence of pyridine.

The results reported here show a striking difference with those obtained in an ACN/pyridine (9:1, *v*/*v*) mixture.[10] Indeed, in pure ACN, $CoBr_2$ is an equilibrium mixture of several cobalt(II) species, whereby Co^{2+} is the most easily reducible one. The reduction of the latter produces a cobalt(I) species that disproportionates too rapidly to further react with aryl halides (ArX). However, we have clearly shown that the presence of $ZnBr_2$ is crucial to stabilize Co^{+} and allow its reaction with ArX. Even though the oxidative addition rate constants of ArX to Co^{I} are smaller than that obtained in ACN/pyridine (9:1), the stabilization of Co^{I} by a zinc(II) species is the key point in the achievement of the electrochemical and chemical cobalt-catalyzed conversions of ArX into organozinc compounds in pure ACN.

Experimental Section

Chemical: Acetonitrile (from SDS) was used without purification. Cobalt bromide (Aldrich), 4-bromoanisole (Aldrich), ethyl 4-bromobenzoate (Aldrich), ethyl 4-iodobenzoate (Aldrich), bromobenzene (Aldrich), methyl 4-chlorobenzoate (Acros), zinc bromide (Fluka), and chlorobenzene (Prolabo) were used as received. $n\mathrm{Bu_4NBF_4}$ (Fluka), used as the supporting electrolyte, was recrystallized from diethyl ether and dried at 60 °C under vacuum.

Instrumentation: Cyclic voltammetry experiments were performed at room temperature (RT) under argon in a three-electrode cell using an EG & G model 273A potentiostat. The reference electrode was an SCE (Tacussel), which was separated from the solution by a bridge compartment filled with the same solvent/supporting electrolyte solution used in the cell. The counter electrode was a platinum or gold grid of about 1 cm^2 apparent surface area. The working electrode was a disk obtained from a cross section of platinum wire (diameter 500 μm or 125 μm) sealed in glass. Zn^{2+} and Co^{2+} were prepared electrochemically in a divided electrochemical cell. The reduction of benzophenone at a known concentration was performed in the cathode compartment, whereas Zn^{2+} and Co^{2+} were generated from the oxidation of a zinc or a cobalt rod in the anode compartment. The weight loss of the anode combined with the charge passed allowed us to determine the concentration of Zn^{2+} and Co^{2+}. Preparative-scale electrolyses to form PhZnBr compounds were carried out in an undivided electrochemical cell with a stainless-steel cathode (20 cm^2) and a zinc rod (1 cm diameter) as the sacrificial anode. A saturated calomel electrode (SCE) was used as the reference. The electrochemical cell was filled with acetonitrile (50 mL) containing $n\text{-}\mathrm{Bu_4NBF_4}$ (0.6 mmol). $CoBr_2$ (1.14 mmol) and PhBr (7.5 mmol) were then added. Electrolyses were performed at constant current ($I = 0.2$ A) under argon and at RT. Reactions were run until complete catalyst loss. The arylzinc species formed was transformed into aryl iodide with the addition of iodine into a sample from the solution. Aryl iodide and bromobenzene were measured by GC with a 5 m DB1 capillary column using tetradecane as the internal reference.

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[1] P. Knochel, R. D. Singer, *Chem. Rev.* **1993**, *93*, 2117.
[2] C. E. Tucker, T. N. Majid, P. Knochel, *J. Am. Chem. Soc.* **1992**, *114*, 3983.
[3] L. Zhu, R. M. Wehmeyer, R. D. Rieke, *J. Org. Chem.* **1991**, *56*, 1445.
[4] R. D. Rieke, *Aldrichimica Acta.* **2000**, *33*, 52.
[5] S. Sibille, V. Ratovelomanana, J. Périchon, *J. Chem. Soc. Chem. Commun.* **1992**, 283.
[6] C. Gosmini, Y. Rollin, J.-Y. Nédélec, J. Périchon, *J. Org. Chem.* **2000**, *65*, 6024.
[7] H. Fillon, E. Le Gall, C. Gosmini, J. Périchon, *Tetrahedron Lett.* **2002**, *43*, 5941.
[8] a) H. Fillon, C. Gosmini, J. Périchon, Patent application in France, no 01/08880, July 4th, **2001**; b) H. Fillon, C. Gosmini, J. Périchon, *J. Am. Chem. Soc.* **2003**, *125*, 3867.
[9] O. Buriez, C. Cannes, J.-Y. Nédélec, J. Périchon, *J. Electroanal. Chem.* **2000**, *495*, 57.
[10] O. Buriez, J.-Y. Nédélec, J. Périchon, *J. Electroanal. Chem.* **2001**, *506*, 162.
[11] J.-M. Duprilot, F. Bedioui, J. Devynck, J.-C. Folest, C. Bied-Charreton, *J. Organomet. Chem.* **1985**, *286*, 77.
[12] C. Cannes, F. Bedioui, S. Condon-Gueugnot, J.-Y. Nédélec, J. Devynck, *New J. Chem.* **1999**, *23*, 489.
[13] A. J. Fry, U. N. Sirisoma, *J. Org. Chem.* **1993**, *58*, 4919.
[14] S. A. Kaufman, T. Phanijphand, A. J. Fry, *Tetrahedron Lett.* **1996**, *37*, 8105.
[15] G. Costa, A. Puxeddu, E. Reisenhofer, *J. Chem. Soc. Dalton Trans.* **1973**, 2034.
[16] A. Puxeddu, G. Costa, N. Marsich, *J. Chem. Soc. Dalton Trans.* **1980**, 1489.

[17] D.-L. Zhou, J. Gao, J. F. Rusling, *J. Am. Chem. Soc.* **1995**, *117*, 1127.

[18] J. F. Rusling, D.-L. Zhou, *J. Electroanal. Chem.* **1997**, *439*, 89.

[19] D. Pletcher, H. Thompson, *J. Electroanal. Chem.* **1999**, *464*, 168.

[20] A. A. Isse, A. Gennaro, E. Vianello, *J. Electroanal. Chem.* **1998**, *444*, 241.

[21] K. S. Alleman, D. G. Peters, *J. Electroanal. Chem.* **1999**, *460*, 207.

[22] L. J. Klein, K. S. Alleman, D. G. Peters, J. A. Karty, J. P. Reilly, *J. Electroanal. Chem.* **2000**, *481*, 24.

[23] R. Scheffold, G. Rytz, L. Walder in *Modern Synthetic Methods*, *Vol. 3* (Ed.: R. Scheffold), Wiley, New York, **1983**, p. 355.

[24] S. Margel, F. Anson, *J. Electrochem. Soc.* **1978**, *125*, 1232.

[25] S. Seka, O. Buriez, J.-Y. Nédélec, J. Périchon, *Chem. Eur. J.* **2002**, *8*, 2534.

[26] a) V. Gutmann, *Coordin. Chem. Rev.* **1967**, *2*, 239; b) W. Grzybkowski, *J. Chem. Soc. Dalton. Trans.* **1987**, 2863.

[27] a) S. I. Ishiguro, H. Nagy, H. Ohtaki, *Bull. Chem. Soc. Jpn.* **1987**, *60*, 2865; b) S. I. Ishiguro, M. Miyauchi, K. Ozutumi, *J. Chem. Soc. Dalton. Trans.* **1990**, 2035.

[28] W. Libus, D. Puchalska, T. Szuchnicka, *J. Phys. Chem.* **1968**, *72*, 2075.

[29] C. Amatore, M. Azzabi, P. Calas, A. Jutand, C. Lefrou, Y. Rollin, *J. Electroanal. Chem.* **1990**, *288*, 45.

[30] C. P. Andrieux, J.-M. Savéant in *Investigation of Rates and Mechanisms of Reactions*, *Vol. 6*, 4th ed, Part 2 (Ed.: C. F. Bernasconi), Wiley, New York, **1986**, Chapter 7.

[31] C. Amatore in *Organic Electrochemistry* (Eds.: H. Lund, M. M. Baizer), Marcel Dekker, New York, **1991**.

[32] For a R value of 0.5, the scan rate v at which the half of Co^I has reacted is easily obtained. From this scan rate, the half-life time ($t_{1/2}$) of Co^I can be deduced, since $t_{1/2} = \Delta E/v$ (with $\Delta E = |E_{R1} - E_{rev}| + |E_{O1} - E_{rev}|$, E_{rev} being the reverse potential). Consequently, the rate constant k_2 for the oxidative addition reaction can be determined ($t_{1/2} = \ln 2/K'$ with $K' = k_2$ [ArX]).

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