Mechanism of the Electrochemical Conversion of Aryl Halides to Arylzinc Compounds by Cobalt Catalysis in DMF/Pyridine

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Abstract: The study of the electrochemical behavior of cobalt bromide, $CoBr_2$, in the presence of zinc bromide, $ZnBr_2$, and aryl halides, ArX, in a dimethylformamide (DMF)/pyridine (9:1, *v*/*v*) mixture allowed us to complete the study of the mechanism of the electrochemical conversion of aryl halides into arylzinc compounds by using cobalt catalysis. The last step of the catalytic process has been shown to be a transmetalation reaction between the arylcobalt(II) species and zinc ions that regenerates the cobalt(II) catalyst. The effect of zinc bromide on each step of the catalytic cycle has been studied. It is especially shown that the presence of $ZnBr_2$ stabilizes the electrogenerated Co^I but has no effect on the rate constant of the oxidative addition of aryl halides, ArX, to Co^I. Rate constants for the disproportionation reaction of Co^I and the oxidative addition have been determined in the presence of $ZnBr_2$ and compared with the values obtained in its absence.

Keywords: arylzinc compounds · cobalt · electrochemistry · kinetics · zinc bromide

Introduction

Organozinc compounds have gained a very significant place in the selective synthesis of carbon–carbon bonds from highly functionalized substrates.[1] However, the chemical preparation of these compounds, especially aryl compounds, is not easily achieved, notably when the aromatic ring bears a reactive functional group such as ketone, ester, or nitrile. In these cases, the preparation of arylzinc compounds from aryl halides is usually achieved by the preliminary formation of aryl-lithium compounds followed by transmetalation with zinc halides. Owing to the low stability of aryl-lithium compounds, these reactions must be performed at −100 °C.[2] Alternatively, the Rieke method, which uses activated zinc obtained by reduction of zinc halide with alkali metal naphthalenide, is convenient with aromatic bromides, even those bearing an electron-withdrawing group.[3]

Some years ago we reported a simple electrochemical preparation of arylzincs using a nickel complex as catalyst along with a zinc sacrificial anode.[4] Nevertheless, this method has some limitations because: i) the low-valent nickel catalyst has to be stabilized by excess bipyridyl ligand, ii) dimethylformamide is the only solvent convenient for these electrosyntheses, and iii) the use of nickel is now discouraged for environmental reasons.

Recently, we have discovered that simple cobalt salts (CoX_2, X = Cl, Br) can be advantageously used instead of nickel complexes as catalysts in the electrochemical conversion of aryl halides to arylzinc compounds.[5] With this new electrochemical method, reactions can be conducted in acetonitrile (ACN) or in dimethylformamide (DMF), and pyridine is used in the place of bipyridine as both ligand and co-solvent. However, the mechanism leading to the formation of arylzinc compounds remains to be elucidated. Thus, we have initiated a program to study this mechanism. In a preliminary investigation we showed that cobalt(I) species electrogenerated from CoX_2 in DMF/pyridine can be stabilized, on the timescale of cyclic voltammetry, with the use of excess pyridine.[6] However, on the timescale of slow cyclic voltammetry or of electrolysis, the cobalt(I) species undergoes a disproportionation reaction leading to solid cobalt along with Co^{II}. By comparison, the reduction of cobalt(II) in the presence of salen, vitamin B_{12}, or bipyridine as ligands leads to a very stable cobalt(I) species.[7–20] Because of its high stability, the cobalt(I) species obtained under these conditions reacts with alkyl and benzylic halides but not with aryl halides. In our case, we showed that the electrogenerated Co^I reacts with aryl halides leading to arylcobalt(III) complexes that are reduced to arylcobalt(II) species at the same potential as $CoBr_2$ (Scheme 1). The rate constant for this oxidative addition mostly depends on the nature of the halogen on the aromatic ring. Thus, we may have competition between the oxidative addition and the disproportionation reaction.

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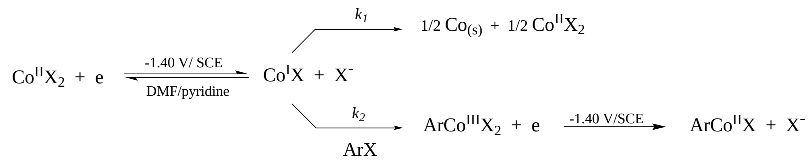


Scheme 1. Reaction of electrogenerated Co^I with aryl halides.

Herein, we report the electrochemical behavior of $CoBr_2$ in a DMF/pyridine (9:1, *v*/*v*) mixture in the presence of zinc bromide and aryl halides. We especially establish a transmetalation reaction between the arylcobalt(II) species and $ZnBr_2$ leading to the arylzinc compound.

Results and Discussion

Study of the electrochemical behavior of $CoBr_2$ in DMF/pyridine (9:1, *v*/*v*) in the presence of $ZnBr_2$. Evidence for the stabilization of the electrogenerated Co^I: The cyclic voltammogram obtained by reduction of $CoBr_2$ in DMF/pyridine at a platinum disk electrode and at $v = 2\ V s^{-1}$ shows a slightly reversible reduction wave at $E_{R1} = -1.4$ V versus SCE (saturated calomel electrode). The backward potential scan exhibits a wave O_2, which corresponds 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).[6] When the voltammogram is recorded with zinc bromide added to the solution, several modifications are observed: i) wave R_1 becomes more reversible and ii) the intensity of O_2 decreases. These could be due to a stabilization of Co^I by $ZnBr_2$. More interestingly, the presence of only bromide ions from nBu$_4$NBr does not lead to a decrease of O_2; this indicates a stabilization of Co^I mainly by zinc ions probably through the formation of a bimetallic "Co–Zn" complex.

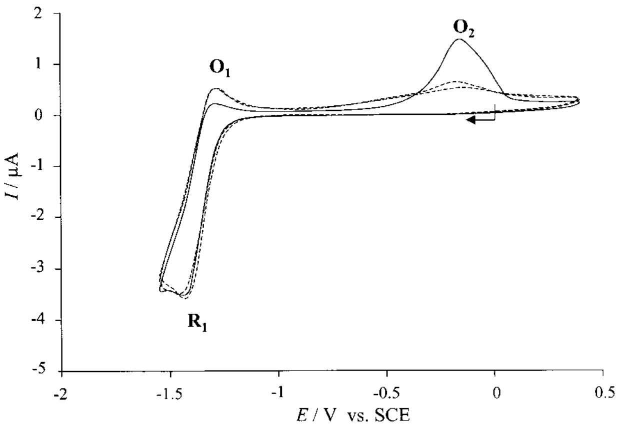


Figure 1. Cyclic voltammograms of $CoBr_2$ (5 mM) in DMF/pyridine (9:1) + NBu_4BF_4 (0.1M) recorded at a platinum disk electrode (0.5 mm diameter) at $v = 2\ V s^{-1}$ and at RT. Complex alone (——) and in the presence of 1 and 2 molar equivalents of zinc bromide (- - - -).

The rate constant for the disproportionation reaction of Co^I can be determined by studying the reversibility of R_1.[21, 22] Figure 2 shows the variation of the peak-current ratio $R = I_{O1}/I_{R1}$ as a function of the scan rate, in which I_{O1} and I_{R1} are the peak current of the oxidation of Co^I and the reduction of Co^{II}, respectively, obtained in the absence and the presence of various amounts of $ZnBr_2$ in the same sweep rate range and at the same electrode. A series of voltammograms has been recorded for 5 mM solutions of $CoBr_2$ containing 1, 2, and 4 molar equivalents of $ZnBr_2$, at scan rates ranging from 0.8 to 25 $V s^{-1}$. For each voltammogram, the degree of reversibility was measured and plotted against the potential scan rate. 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, $t_{1/2}$, 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_I for the disproportionation reaction can be determined ($t_{1/2} = (k_I \cdot [Co^I]_0)^{-1}$). Table 1 shows that the presence of one molar equivalent of $ZnBr_2$ relative to $CoBr_2$ leads to a halving of the rate constant k_I. In the presence of two and four molar equivalents of $ZnBr_2$ the rate constant keeps decreasing but more slowly.

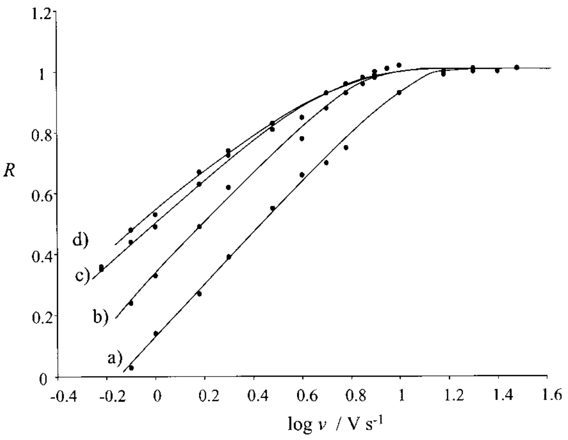


Figure 2. Variation of the peak current ratio $R = I_{O1}/I_{R1}$ as a function of log$v$ (potential scan rate in $V s^{-1}$) for $CoBr_2$ (5 mM) in DMF/pyridine (9:1, *v*/*v*) + NBu_4BF_4 (0.1M); a) complex alone and in the presence of b) one, c) two, and d) four molar equivalents of zinc bromide.

Table 1. Effect of the zinc bromide amount on the rate constant for the disproportionation reaction of the electrogenerated Co^I in DMF/pyridine (9:1, *v*/*v*) + NBu_4BF_4 (0.1M); $[CoBr_2] = 5$ mM.

$[ZnBr_2]$[mM]	k_I [$M^{-1}s^{-1}$]
0	2000 ± 500
5	1000 ± 250
10	700 ± 150
20	500 ± 120

The stability of Co^I in the presence of $ZnBr_2$ was then studied in preparative-scale electrolyses leading to organozinc compounds. We decided to use PhCl as the aryl halide because, in this case, the rate for the disproportionation reaction of Co^I ($k_I = 2000 \pm 500\ M^{-1}s^{-1}$) is much faster than the oxidative addition rate of PhCl to Co^I ($k_2 = 120 \pm$

$15\,\text{M}^{-1}\,\text{s}^{-1}$)[6] and the balance between the two processes can be easily studied. Experiments were conducted at a constant current ($I = 0.2$ A), as described in the Experimental Section. As shown in Table 2, the presence of increasing amounts of zinc bromide leads to a larger consumption of PhCl in agreement with a better stabilization of the catalyst Co^I. However, above 5 molar equivalents of $ZnBr_2$ relative to $CoBr_2$, the consumption of PhCl does not increase any more. As expected, increasing amounts of $ZnBr_2$ lead to an increase in the arylzinc PhZnCl yield. Alternatively, $ZnBr_2$ can be electrochemically generated from the electroreduction of 1,2-dibromoethane in the presence of a sacrificial zinc anode. In this case, the same results were obtained.

Table 2. Preparative scale electrolyses. Effect of the zinc bromide amount on the consumption of PhCl and the formation of PhZnCl in DMF/pyridine (9:1, *v*/*v*); $[CoBr_2] = 23$ mM.

$[ZnBr_2]$[mM]	PhCl recovered [%]	PhZnCl [%]
0	48	25
115	15	45
230	18	60

Kinetic investigations for the reaction between the electrogenerated Co^I and aryl halides in the presence of $ZnBr_2$: Since zinc bromide can stabilize the electrogenerated Co^I species, we were interested in a possible effect of $ZnBr_2$ on the rate of oxidative addition of ArX to Co^I. A study by cyclic voltammetry shows that addition of aryl halides to a solution containing $CoBr_2$ (5 mM) and $ZnBr_2$ (5 and 10 mM) leads to a decrease in the intensity of O_1 (oxidation wave of Co^I); this indicates a reaction between the electrogenerated Co^I and ArX leading to the corresponding arylcobalt(III) complex.

The efficiency of this oxidative addition has been quantified from the ratio $R' = I_{ArX}/I_0$, where I_{ArX} and I_0 are the peak current of the oxidation wave O_1 (oxidation of Co^I produced in R_1) in the presence and absence of ArX, respectively, at the same sweep rate and on the same electrode.[21–22] A series of voltammograms has been recorded for 5 mM solutions of $CoBr_2$ in the absence and presence of $ZnBr_2$ (5 and 10 mM) at scan rates ranging from 5 to 30 $\text{V}\,\text{s}^{-1}$, and at concentrations of ArX from 2.5 to 145 mM. For each experiment the ratio R' was measured, and the corresponding set of values plotted against [ArX]/v (Figure 3 for 2-bromomesitylene). All the experimental data fit onto a single curve; this demonstrates the absence of any effect of zinc bromide on the oxidative addition rate of ArX to Co^I. Similar results were obtained with various aryl halides. From a ratio $R' = 0.5$, the rate constant for the oxidative addition is determined through the half-life of the Co^I species. The results are summarized in Table 3.

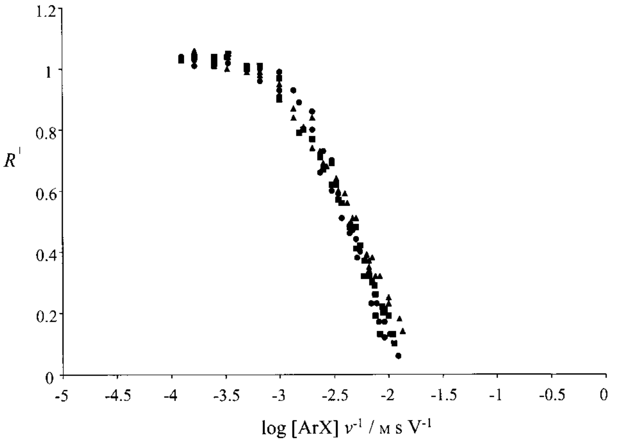
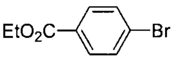
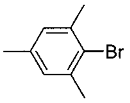
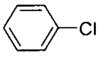


Figure 3. Efficiency of the oxidative addition from the variation of the peak current ratio $R' = I_{ArX}/I_0$ as a function of log ([ArX]/v), $5 < v < 20\ \text{V}\,\text{s}^{-1}$ and $5 < [ArX] < 850$ mM for $CoBr_2$ (5 mM) and ArX = 2-bromomesitylene in DMF/pyridine (9:1, *v*/*v*) + NBu_4BF_4 (0.1M); in the absence (●) and the presence of one (■) and two (▲) molar equivalents of zinc bromide.

Table 3. Effect of $ZnBr_2$ on the rate constants for the oxidative addition of ArX to Co^I for various aryl halides in DMF/pyridine (9:1, *v*/*v*) + NBu_4BF_4 (0.1M); $[CoBr_2] = 5$ mM.

ArX	k_2 [$\text{M}^{-1}\text{s}^{-1}$] In the absence of $ZnBr_2$	 In the presence of $ZnBr_2$ [10 mM]
	7500 ± 860	6040 ± 1040
	470 ± 60	530 ± 40
	120 ± 20	170 ± 30

Evidence of a transmetalation reaction between arylcobalt(II) species and zinc bromide: As already shown,[6] the arylcobalt(III) complex resulting from the reaction between Co^I and ArX is reduced at the level of R_1 leading to the arylcobalt(II) complex. Furthermore, the method[23] combining chronoamperometry and steady-state voltammetry at a rotating disk electrode to determine the absolute number of electrons n involved in an irreversible wave was applied to the reduction of $Co^{II}Br_2$ in the presence of 50 molar equivalents of ethyl 4-bromobenzoate and in DMF/pyridine. We established that wave R_1 is bielectronic ($n = 2$). Thus, the addition of ArX to a solution containing Co^{II} leads to an increase in the intensity of R_1 up to a limiting current corresponding to two electrons. Actually, this is not observed at high and low sweep rates ($v > 30$ and $v < 0.15\ \text{V}\,\text{s}^{-1}$). Indeed, in the former case, the oxidative addition and the disproportionation reaction are both kinetically frozen, and therefore the number of electron involved in R_1 is constant and equal to one. Conversely, in the second case, the number of electrons involved in R_1 is already close to two before the addition of ArX since the disproportionation reaction has enough time to operate. In the presence of ArX and at low sweep rates, the number of electrons involved in R_1 remains constant and equal to two but the second electron is involved in both the reduction of the arylcobalt(III) complex and the reduction of the regenerated Co^{II} via the disproportionation reaction. Because of the competition between the disproportionation reaction and the oxidative addition (Scheme 1), the distribution of the second electron thus depends on the nature of ArX. For instance, in the presence of excess ethyl 4-bromobenzoate as the aryl halide, the second electron uptake is due to the reduction of the arylcobalt(III) complex into the arylcobalt(II) complex. In this case, the oxidative addition reaction is very rapid, and the disproportionation reaction can be disregarded. Thus, the addition of ethyl 4-bromobenzoate at low sweep rates does not lead to an increase of the intensity of R_1 whereas the oxidation wave O_2 totally disappears (Figure 4). However, if under these conditions increasing amounts of $ZnBr_2$ are added to the solution, the peak current of R_1 increases (Figure 5). We can rule out the possible reduction of $ZnBr_2$, which would occur at a potential negative to the reduction of $CoBr_2$ ($E = -1.7$ V). Indeed, this would result in an oxidation wave located at $E = -0.8$ V on the cyclic voltammogram and corresponding to the oxidation of solid zinc deposited at the electrode surface.

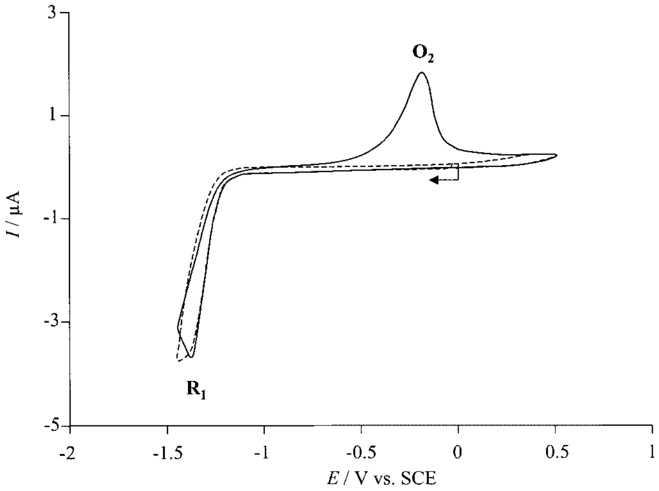


Figure 4. Cyclic voltammograms of $CoBr_2$ (5 mM) in DMF/pyridine (9:1) + NBu_4BF_4 (0.1M) recorded at a platinum disk electrode (0.5 mm diameter) at $v = 0.2\ Vs^{-1}$ and at RT. In the absence (——) and in the presence of ethyl 4-bromobenzoate (50 mM) (----).

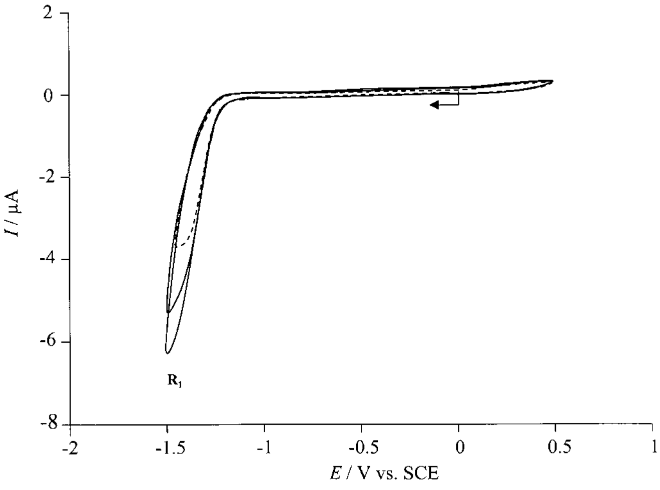
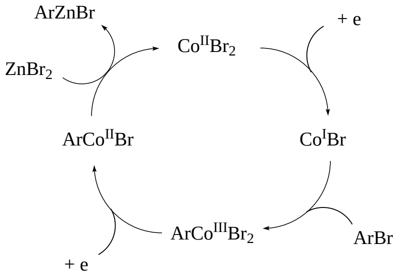


Figure 5. Cyclic voltammograms of $CoBr_2$ (5 mM) in the presence of ethyl 4-bromobenzoate (50 mM) in DMF/pyridine (9:1) + NBu_4BF_4 (0.1M) recorded at a platinum disk electrode (0.5 mm diameter) at $v = 0.2\ Vs^{-1}$ and at RT. In the absence (----) and in the presence of zinc bromide (10 and 20 mM (——)).

Consequently, the observed catalytic current can only be due to the regeneration of Co^{II} after a transmetalation reaction between $ArCo^{II}Br$ and $ZnBr_2$.

This result allows us to propose a catalytic cycle for the electrochemical conversion of aryl halides to arylzinc compounds in a DMF/pyridine mixture. The cycle is initiated by the reduction of $Co^{II}Br_2$ to $Co^{I}Br$, which undergoes an oxidative addition with aryl halides to afford the trivalent cobalt complex $ArCo^{III}Br_2$. This is reduced to $ArCo^{II}Br$ by a single electron uptake at the same potential at which $Co^{II}Br_2$ is reduced. The cycle is closed by a transmetalation reaction between $ArCo^{II}Br$ and $ZnBr_2$ that leads to the arylzinc compound and the starting divalent cobalt (Scheme 2).



Scheme 2. Proposed mechanism for the electrochemical conversion of aryl halides to arylzinc species in DMF/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.

Conclusion

The electrochemical conversion of aryl halides to arylzinc compounds by cobalt catalysis proceeds from the reduction of $Co^{II}Br_2$ by a chain process involving an $ArCo^{III}Br_2$ intermediate as well as $Co^{I}Br$ and $ArCo^{II}Br$ complexes. The various steps allowing the catalytic chain shown in Scheme 2 to propagate have now been identified. In this paper, we have especially focused on the electrochemical behavior of $CoBr_2$ in the presence of zinc bromide in a DMF/pyridine mixture, and thus evidenced the last step of the catalytic cycle as being a transmetalation reaction between the arylcobalt(II) complex and $ZnBr_2$ that regenerates the cobalt(II) catalyst precursor. Furthermore, we have demonstrated that the presence of zinc bromide stabilizes the electrogenerated Co^{I} species; this leads to an increase in the catalyst turnover and a decrease in the catalyst loss through the disproportionation reaction. However, the presence of zinc bromide has no effect on the oxidative addition rate of ArX to Co^{I}.

Experimental Section

Chemicals: Dimethylformamide (from SDS) was used without purification. Pyridine was dried over KOH. Cobalt bromide (Aldrich), 2-bromomesitylene (Aldrich), ethyl 4-bromobenzoate (Aldrich), 4-bromoanisole (Aldrich), and chlorobenzene (Prolabo) were used as received. nBu_4NBF_4 (Fluka), used as the supporting electrolyte, was dried at 60 °C under vacuum. Zinc bromide (Fluka) was used as received or dried at 60 °C under vacuum. Iodine resublimed (Acros) was used as received.

Instrumentation: Cyclic voltammetry experiments were performed at room temperature under argon in a three-electrode cell. 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) sealed in glass.

An EG&G model 273A potentiostat or an EG&G PAR175 signal generator linked to a home-made potentiostat with a positive feedback loop for ohmic drop compensation was used.[24]

Preparative-scale electrolyses to form PhZnCl 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. An SCE was used as the reference. The electrochemical cell was filled with nBu$_4$NBF$_4$ (0.6 mmol) in DMF (45 mL) and pyridine (5 mL). CoBr$_2$ (1.14 mmol) and PhCl (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 by the addition of iodine into the solution. Aryl iodide was measured by GC with a 5 m DB1 capillary column and tetradecane as the internal reference.

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