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Nickel-Catalyzed Electrochemical Reductive Relay Cross-Coupling of Alkyl Halides to Aryl Halides

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Abstract: A Highly regioselective Ni-catalyzed electrochemical reductive relay cross-coupling between an aryl halide and an alkyl halide has been developed in an undivided cell. Various functional groups are tolerated under this mild reaction conditions, which provides an alternative approach for the synthesis of 1,1-diarylalkanes.

Nickel-catalyzed cross-coupling reactions of organometallic reagents and organic electrophiles have emerged as powerful synthetic tools for forging C(sp²)-C(sp³) bonds.^[1] Recently, substantial effort has also been spent on the development of nickel-catalyzed reductive cross-coupling reactions between aryl electrophiles and alkyl electrophiles, wherein organometallic reagents is avoided.^[2] For instance, in 2010 Weix and coworkers reported efficient Ni-catalyzed cross-couplings of aryl halides with unactivated alkyl halides using Mn as the reductant (Scheme 1a).^[3] Inspired by this seminal work, many Ni-catalyzed reductive cross-couplings between aryl halides and alkyl halides have been developed, including asymmetric variants.^[4,5] However, these reactions require a metal reductant (typically Mn or Zn) to regenerate the Ni catalyst. The use of stoichiometric metal additives has some drawbacks: 1) the metal reductant (typically a powder) often requires surface activation; 2) the reactivity could vary depending on the source of the metal powder; 3) some functional groups react readily with Zn or Mn. To circumvent such issues, the use of organic or inorganic reductants^[6] and photoredox catalysis have emerged as popular strategies.^[7] Alternatively, Ni-catalyzed electrochemical reductive coupling could provide an attractive solution, whereby electric current is used to turn over the Ni catalysis.^[8,9] However, electrocatalysis aside, reductive cross-coupling of aryl halides and unactivated alkyl halides is inherently challenging due to the difficulty of obtaining selectivity for the cross-coupled product over homo-coupled products.^[10,11] Recently, Hansen and coworkers reported Ni-catalyzed electrochemical cross-coupling of aryl bromides and unactivated alkyl bromides using 4-4'dimethoxy-2-2'-bipyridine (dmbpy) or amidine-based ligands with Zn as a sacrificial anode.^[12] However, to the best our knowledge, Ni-catalyzed electrochemical reductive relay cross-coupling of aryl bromides and alkyl bromides is unknown. Such a transformation would be valuable for the construction of 1,1diarylalkanes, which are common structural motifs in many natural products and biologically active compounds.[13]

As part of our ongoing interest in metal-catalyzed electrochemistry^[14] and 1,1-diarylalkane synthesis,^[15] we questioned whether electrochemical reductive relay cross-

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coupling of alkyl bromides and aryl bromides could take place by taking advantage of "chain-walking" of an alkyl-nickel species.^{[16– ^{19]} Herein, we report the first such example of Ni-catalyzed electrochemical relay cross-coupling of aryl halides and alkyl bromides, affording 1,1-diarylalkanes with good to excellent selectivity and yield (Scheme 1b). This envisioned transformation is challenging as a result of a multitude of undesired side reactions, including those depicted in path a, b, and c (Scheme 1c).}



Scheme 1. Reductive Cross-Coupling Reactions

Initially, we probed various reaction conditions using 4bromoanisole (1a) and (2-bromoethyl)benzene (2a) as reaction partners. To our delight, using Ni(ClO₄)₂•6H₂O as precatalyst, 2,9-dimethyl-1,10-phenanthroline (Ligand 1) as the ligand, n-Bu₄NBr as the electrolyte, and N,N-dimethylacetamide (DMA) as the solvent in an undivided cell with iron and Ni foam as electrodes under 6 mA current for 10 hours at room temperature, the relay cross-coupling product was obtained in a good isolated yield of 80% (Table 1, entry 1). Using Nil₂ as catalyst resulted in a slightly lower yield (entry 2). When using reticulated vitreous carbon (RVC) instead of Ni foam as the cathode, the yield decreased to 74% (entry 3). In addition, when we replaced iron with magnesium as the sacrificial anode, the efficiency of the reaction decreased precipitously (entry 4). Increasing or decreasing the amount of 2a gave lower yields (entries 5 and 6). Similar outcomes were also obtained when changing the electric current to 4 mA or 8 mA (entries 7 and 8). It is worth noting that the methyl groups on the ligand L1 and L2 (entry 9) are crucial for the reaction (see Table S1 in the Supporting Information for details). A control experiment revealed that no coupling product was produced in the absence of the catalyst or ligand (entry 10).

With the optimized reaction conditions in hand, we investigated the generality of this electrochemical reductive coupling reaction. As shown in Scheme 2, the catalytic system exhibited good functional group tolerance. Arenes substituted

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Table 1. Reaction Optimization with Substrate 1a[a]



[a] Standard conditions: **1a** (0.3 mmol), **2a** (1.5 equiv), Ni(ClO₄)₂·6H₂O (10 mol%), Ligand (12 mol%), *n*·Bu₄NBr (1.0 equiv), and DMA (4 mL), in an undivided cell with iron (1.5 × 0.5 cm²) and Ni foam (2.5 × 1.5 cm²) as electrodes, rt, 6.0 mA, 10 h. [b] The yield was determined by ¹H NMR using CH₂Br₂ as an internal standard. [c] Isolated yield in parentheses.

with a variety of functional groups such as alkyl, ether, trifluoromethyl, and alkenyl groups were well tolerated affording good to excellent yields (3a-3e, 3p). For those substrates bearing more reactive groups such as hydroxyl, amino or protected amino groups (3f-3l), the electrochemical reductive relay cross-coupling reactions can proceed smoothly, with good yields. A morpholine group substituted on the aromatic ring is tolerated as well (3m). In addition, for di- or tri-substituted arenes, the reaction can also deliver acceptable yields (3n-3r). Encouragingly, when we investigated the corresponding aryl chlorides, the reductive relay cross-coupling reaction can proceed well with good to excellent yields. Acetyl, ester, nitrile, and sulfonyl groups on said substrates can be well tolerated, affording good to excellent yields (3s-3w, 3y). In addition, quinoline is also well tolerated in this electrochemical method (3x). Commercially available pharmaceuticals like fenofibrate, a medicine used to treat or prevent cardiovascular disease participated smoothly in the electrochemical reductive coupling, affording the indicated product (3z) in excellent yield at both 0.3 mmol and 3.0 mmol scale, thus demonstrating the synthetic potential of this protocol. Unfortunately, electron-rich aryl chlorides are not effective (e.g. chloroanisole).

Next we moved to examine the scope of the alkyl bromide. As shown in Scheme 3, alkyl bromides substituted with a variety of functional groups such as chloro, fluoro, ether, and hydroxyl were well tolerated under the standard reaction conditions, affording the relay products in good yields (4a-4g). To our delight, this relay process can matriculate along three or four carbon-length chains with only slightly diminished yield (4h and 4i). In addition, even a secondary alkyl bromide is a suitable partner under the standard conditions, affording the corresponding product in satisfactory yield (4h).

To gain insight into the reaction mechanism, we conducted a series of cyclic voltammetric analyses (Figure 1, 2, and S2–S8, Supporting Information). Compared to the substrates, the nickel

catalyst is more easily reduced to a lower valency (Figure S2). When the ligand is present, the complex exhibits two quasireversible reductive peaks at -1.29 V and -1.82 V versus Ag/AgNO₃ in dimethylacetamide (curve d, Figure 1), which may be attributed to the reductive potential of Ni(II)/Ni(I) and Ni(I)/Ni(0), respectively. Indeed, the controlled potential electrolysis (E = -1.5 V) does not afford the desired product, whereas the product is obtained in 10% yield at lower potential (E = -1.9 V). In addition, the yield can be increased to 50% when five times the amount of electricity is passed (Scheme 4). These results indicate that the Ni(0) complex is generated at the cathode and acts as the active catalyst. In addition, in the absence of electricity, the stoichiometric reaction with Ni(cod)₂ as catalyst can afford the desired product in 25% yield (Scheme 5).



Scheme 2. Evaluation of Arene Scope

We then sought to understand which substrates the catalyst prefers to react with. To our delight, catalytic currents were observed when either of the two substrates were added into the mixture of nickel catalyst and ligand. In addition, when an activated aryl bromide was added, the current was significantly increased (Figure S3–S5). When the alkyl bromide (**2a**) was added first, the catalytic current was slightly increased whereas the catalytic current was significantly increased (about six fold)

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after the addition of aryl bromide **1a** (Figure 2). Furthermore, when the aryl bromide **(1)** was added first, the catalytic current is significantly increased whereas the catalytic current was slightly increased (only one-seventh) following the subsequent addition of alkyl bromide **2a** (Figure S6). This phenomenon was much more obvious when an activated aryl bromide was used (Figure S7–S8). Based on the above cyclic voltammetric (CV) studies, the putative Ni(0) complex reacts more readily with an aryl bromide.



PMP = 4-methoxylphenyl.

Scheme 3. Evaluation of Alkyl Halides



Figure 1. Cyclic voltammograms recorded on a glassy carbon electrode at 100 mVs⁻¹. (a) DMA containing 0.1 M of *n*-Bu₄NBr; (b) solution (a) with 5 mM of Ni(ClO₄)₂•6H₂O added; c) solution (a) with 5 mM of 2,9-Dimethyl-1,10-phenanthroline added. d) solution (a) with 7.5 mM of Ni(ClO₄)₂•6H₂O and 2,9-Dimethyl-1,10-phenanthroline (Ni/L = 1/1) added.



Scheme 4. Controlled Potential Electrolysis



Scheme 5. Stoichiometric Reaction Without Electric Current



Figure 2. Cyclic voltammograms recorded on a glassy carbon electrode at 100 mVs-1. (A): (a) DMA containing 0.1 M of *n*-Bu₄NBr; (b) solution (a) with 7.5 mM of Ni(ClO₄)₂•6H₂O and Ligand 1 added; (c) solution (b) with 10 mM of **2a** added; (d) solution (c) with 10 mM of **1a** added.

Based on literature reports^[20] and our mechanistic studies (see Supporting Information for more details), a plausible mechanism is presented for the Ni-catalyzed electrochemical reductive couplings (Scheme 6). First, the Ni(II) catalyst is reduced to Ni(0) (**A**) via cathodic reduction. Then, after oxidative addition of an aryl bromide to Ni(0), aryl Ni(II) species (**B**) is formed, which can react with an alkyl radical to generate a Ni(III) species (**C**). Direct reductive elimination from **C** can generate a linear by-product, **C** can also be converted into species **E**, a more thermodynamically stable benzylic Ni(III) intermediate via multiple β -hydride elimination/reinsertion steps. Upon reductive elimination, the desired cross-coupling product and a Ni(I) species (**F**) are formed. By single electron transfer and cathodic reduction, the active Ni(0) is then regenerated.



Scheme 6. Plausible Catalytic Cycle

In summary, we have demonstrated the first example of a Nicatalyzed electrochemical reductive relay cross-coupling of aryl

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bromides or chlorides to alkyl bromides in an undivided cell, affording 1,1-diarylalkanes with good yields and regioselectivities. The protocol is operationally simple and robust. Further research to explore the mechanism and to develop more transition metal-catalyzed electrochemical reductive relay cross-couplings is currently underway in our laboratory.

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Keywords: Organic electrochemistry • reductive relay crosscoupling • nickel • 1,1-diarylalkanes

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