Nickel-catalyzed electrochemical carboxylation of unactivated aryl and alkyl halides with CO₂

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Electrochemical catalytic reductive cross couplings are powerful and sustainable methods to construct C–C bonds by using electron as the clean reductant. However, activated substrates are used in most cases. Herein, we report a general and practical electro-reductive Ni-catalytic system, realizing the electrocatalytic carboxylation of unactivated aryl chlorides and alkyl bromides with CO₂. A variety of unactivated aryl bromides, iodides and sulfonates can also undergo such a reaction smoothly. Notably, we also realize the catalytic electrochemical carboxylation of aryl (pseudo)halides with CO₂ avoiding the use of sacrificial electrodes. Moreover, this sustainable and economic strategy with electron as the clean reductant features mild conditions, inexpensive catalyst, safe and cheap electrodes, good functional group tolerance and broad substrate scope. Mechanistic investigations indicate that the reaction might proceed via oxidative addition of aryl halides to Ni(0) complex, the reduction of aryl-Ni(II) adduct to the Ni(I) species and following carboxylation with CO₂.
Reductive cross couplings represent powerful methods to generate C–C bonds by circumventing extra synthetic steps and handling moisture-sensitive organometallic reagents. Much progress has been achieved in last decades via transition metal catalysis and photocatalysis. Recently, significant advance of electrochemistry has attracted much attention with electron as clean reductant, providing a sustainable solution for chemical synthesis. Compared to direct electrochemistry, electrocatalysis is more attractive and useful due to the lower potential and better functional group tolerance. Notably, electrochemical transition metal-catalysis, is efficient and powerful in reductive cross couplings. Electro-reductive Ni-catalyzed coupling of aryl halides with organo (pseudo)halides and carbonyl-containing compounds has emerged as a convenient strategy. However, most of such cases are limited to activated aryl halides, which bear electron-withdrawing groups (EWGs) or electron-poor heteroarenes. The electrocatalytic reductive cross couplings of unactivated aryl halides, especially unactivated aryl chlorides, are challenging tasks to resolve.

Carboxylation of organohalides with CO$_2$ is a direct and effective way to construct valuable carboxylic acids due to the abundant, nontoxic and recyclable properties of CO$_2$. However, the thermodynamic stability and kinetic inertness make it difficult to achieve high efficiency under mild reaction conditions. It is even more challenging when the inexpensive coupling partners are less reactive. Although recent progress has shown some robust catalytic manners in transition-metal catalysis and photocatalysis, the use of stoichiometric amount of extra metallic reductants, expensive Ir-photosensitizer, or reactive organohalides still limits their wide application. Meanwhile, electrocatalytic carboxylation of activated aryl (pseudo)halides has rarely been realized, which are more challenging due to the low reactivity of both unactivated organohalides and CO$_2$ as well as many competing side reactions, such as protonation, β-H elimination, migration, and homodimerization of the generated organometallic reagents and electrochemical decarboxylation of the products. Besides the limitations in substrate scope, the reductive electrochemical carboxylations mainly rely on the use of sacrificial electrodes.

Here, we show a general and practical electrochemical Ni-catalytic system, realizing the electrocatalytic carboxylation of challenging aryl chlorides and unactivated alkyl bromides with CO$_2$. A variety of unactivated aryl bromides, iodides, and sulfonates also undergo such a reaction smoothly. Moreover, the catalytic electrochemical carboxylation of aryl (pseudo)halides with CO$_2$ avoiding the use of sacrificial electrodes is also developed.

Results

Optimization of Ni-catalyzed electrochemical carboxylation. We initiated our studies by exploring electro-reductive Ni-catalyzed carboxylation of 4-chlorobiphenyl 1a with CO$_2$ (see Supplementary Table 1). Considering that aryl chlorides are less reactive than aryl bromides or iodides, we proposed that a highly reactive Ni-catalytic system should be developed to improve the challenging oxidative addition under mild reaction conditions. We decided to explore proper ligand to keep the Ni-catalyst active and increase the catalytic efficiency. After systematic condition screening, we were delighted to realize the carboxylation of 1a to give 2a in 70% yield in the undivided cell by using Ni-catalyst and mixed nitrogen ligands, which contained diterbutylbipyridine (L, dtbbpy) and 4-dimethylaminopyridine (DMAP) (Supplementary Table 1, entry 1). Both of these two ligands were important as no or low efficiency was observed in the absence of either one (Supplementary Table 1, entries 2 and 3). Besides, Lewis acidic MgBr$_2$ also promoted the reaction (Supplementary Table 1, entry 4), which might coordinate with CO$_2$ and increase its electrophilicity. Control experiments verified the essential role of nickel catalyst, CO$_2$, and electricity (Supplementary Table 1, entries 5–7). The use of potassium tert-butoxide (KO’Bu) had improvement for the carboxylation (Supplementary Table 1, entry 8). Supporting electrolyte also had a significant effect on the reaction (Supplementary Table 1, entry 9). Varying from other parameters, such as solvent and electric current, did not give better results (Supplementary Table 1, entries 10–12).

Substrate scope. With the optimal reaction conditions in hand, we first explored the scope of aryl chlorides (Fig. 2). A variety of unactivated aryl chlorides underwent the carboxylation smoothly to give the desired acids in moderate to good yields (1a–1f). Notably, the substrate 1c bearing free alcohol, which might undergo oxidation via β-H elimination or coupling via C–O bond activation, was not reported in previous carboxylations with CO$_2$. Deactivated aryl chlorides (1e and 1f) bearing with electron-donating groups at the para position, which show no or lower reactivity in previous carboxylations, were also amenable to our reaction. Notably, clofibrate (1f), a commercially available drug, underwent the reaction to afford 2f in 53% yield, which might be applied in drug discovery to improve...
the hydrophilicity and metabolism of drug molecules. As electron-deficient aryl chlorides were more reactive coupling partners, they could take part in the reaction with lower catalyst loading and temperature in the absence of either DMAP or MgBr₂. Notably, this electrochemical approach exhibited good tolerance to diverse functional groups, including hydroxyl (1c), fluoro (1d), methoxyl (1e), and ketone (1f and 1j). Besides substituted phenyl chlorides, 2-naphthyl and more sterically hindered 1-naphthyl chlorides were also suitable substrates in our reaction. The substrates with more steric hindrance, such as 2-methylphenyl chloride, were unreactive in our case, which might arise from more difficult oxidative addition of C–Cl bonds.

We further examined carboxylation of other unactivated aryl (pseudo)halides (Fig. 2). Besides simple phenyl bromide 3a, a wide range of para- and meta-substituted aryl bromides (3b–3m) reacted well with CO₂ to afford the desired carboxylic acids in good yields. Interestingly, the sterically hindered aryl...
bromide 3n bearing ortho phenyl group could also undergo the carboxylation in moderate efficiency. Moreover, the carboxylation of di-substituted phenyl (3o, 3p) and fused (hetero)aryl bromides (3r–3t) was also smooth. Deactivated aryl bromides (3c, 3e, 3j, 3k, 3p–3t) bearing EDGs were also reactive in this process to give desired carboxylic acids in good yields. A set of functional groups, such as ether (3c, 3d, 3f), thioether (3g), ester (3h), alkene (3i), acetal (3m) and heterocycles (3r–3t), were well tolerated. Besides aryl bromides, aryl iodides (3u–3w) also underwent the carboxylation smoothly. Moreover, aryl sulfonates (3x–3ab), such as a mesylate, tosylates, and triflates, which are easily available from phenols, also showed high reactivity and selectivity in this reaction.

Furthermore, we investigated more challenging carboxylation of unactivated alkyl bromides to give important alkyl carboxylic acids. To our delight, a range of primary alkyl bromides (5a–5g) could afford the corresponding carboxylic acids in moderate to good yields with good functional group tolerance under slightly modified conditions (Fig. 3). Moreover, unactivated cyclic alkyl bromides (5h and 5i) could also take part in this reaction to generate carboxylic acids with synthetically useful yields, although these substrates were considered as challenging coupling partners in carboxylation events^45,46.

Mechanistic studies. To gain more insight into the reaction mechanism, we first applied the synthesized complex LNi(acac)2 as pre-catalyst in the carboxylation of 3 h (Fig. 5a), which provided 4 h in a similar yield to that of standard reaction and higher than that obtained with Ni(COD)2 and dtbbpy (Fig. 5b). Moreover, we carried out the stoichiometric reaction of 3ac with Ni-catalyst to generate an oxidative addition adduct 1-1 (Fig. 5c), which showed similar catalytic activity (Fig. 5d), indicating that 1-1 might be the key intermediate in the catalytic cycle. In addition, the complex 1-2 [ArNi(dtbbpy)(DMAP)Cl] was detected in the catalytic reaction (Fig. 5e).

Furthermore, we also tested electrochemical analysis and UV-vis spectroscopy (Fig. 6). We found that both the cyclic voltammogram (CV) and absorption spectra of LNi(acac)2 were almost consistent with the mixture of Ni(acac)2 and dtbbpy in NMP solution (Fig. 6a, b), suggesting that pre-catalyst LNi(acac)2 was formed in situ by mixing Ni(acac)2 and dtbbpy by a ratio of 1:1 in NMP solution. All these results indicated that the coordination occurred between nickel catalyst and ligand. Besides, such nickel catalytic systems had two irreversible reductive peaks in the CV tests (Fig. 6a), which indicated that nickel catalysts were reduced into Ni(I) and Ni(0) species on the cathodic surface.

We continued to conduct CV tests for Ni(acac)2 and dtbbpy in the presence of 3 h (Fig. 7a) and found a steep reductive peak at −2.73 V (E0), which indicated a typical catalytic current. Similarly strong catalytic current could also be observed when LNi(acac)2 was used in place of Ni(acac)2 and dtbbpy. Since the pre-formed nickel complex could be reduced into its Ni(0) form according to cyclic voltammetric results, we inferred that the
Responsive catalytic current was attributed to oxidative addition between 3h and Ni(0) complex. After the introduction of CO₂, the reductive peak current was further increased, indicating the carboxylation reaction occurred. Besides, the deactivated aryl bromide 3b, which is reduced at −2.64 V (E_p), showed the rise of its peak current in the Ni-catalytic system along with DMAP (Fig. 7b), suggesting that DMAP improved the Ni-catalytic efficiency in activating inert aryl bromide to reaction with nickel catalyst. CV test of adduct 1−1 was also investigated in NMP solution to show two irreversible reductive peaks, which might correspond to the reduction of adduct 1−1 at the cathodic surface (Fig. 7c)62. Furthermore, two new reductive peaks at −1.86 V (E_p) and −2.27 V (E_p) were emerged when adduct 1−1 was present in the CO₂ atmosphere, which might indicate that oxidative addition complex 1−1 was reduced into its Ni(II) species, which then underwent carboxylation with CO₂ and was further reduced into Ni(0) species63. All of the results indicated that adduct 1−1 was generated during the electrolytic process and then reduced to Ni(II) species which underwent carboxylation with CO₂.

Based on these results and the previous work15−20,31−38,64, a possible catalytic cycle was proposed (Fig. 8). First, the L⁶Ni(0)
species A is generated from the complex Ni(acac)_2 in the presence of bipyridine ligand and DMAP on the cathode. Then the oxidative addition between A and the aryl halide occurred to yield the adduct B, which would be further reduced to Ni(I) species C by cathode. Then, C reacted with CO_2 to give the nickel carboxylate intermediate D. Following ligand exchange and reduction of nickel carboxylate complex regenerated the active Ni(0)-catalyst A and afforded carboxylate, which would undergo protonation to give the desired product.

**Discussion**

In this work, we have developed a general and practical electroreductive Ni-catalytic system, realizing the electrocatalytic carboxylation of challenging, unactivated aryl chlorides and alkyl bromides with CO_2. Unactivated aryl bromides, iodides, and sulfonates can also undergo such an electrocatalytic carboxylation smoothly. The use of DMAP as additional ligand and MgBr_2 as Lewis acid improved the efficiency for the electrocarboxylation of unactivated aryl halides. Notably, we also realize the catalytic electrochemical carboxylation of aryl (pseudo) halides with CO_2 avoiding the use of sacrificial electrodes. This protocol is operationally simple and robust with mild conditions, undivided cell, safe and cheap electrodes, good functional group tolerance, and broad substrate scope. Mechanistic investigations indicate that the reaction might proceed via oxidative addition of aryl halides to LnNi(0), further reduction to the Ni(I) species, and following carboxylation with CO_2. More application
Methods
Synthesis of 1a–1f, 1i–1l, 3a–3c, 3e, 3i–3l, 3p, 3s, and 3aa. In a 50 mL three-neck flask equipped with a carbon felt cathode and a Zn plate, aryl halides (0.3 mmol), NiBr₂·DME (0.03 mmol, 10 mol%), 4,4′-di-tert-butyl-2,2′-bipyridine (0.03 mmol, 10 mol%), DMAP (0.06 mmol, 20 mol%), KOtBu (0.15 mmol, 0.5 equiv), anhydrous MgBr₂ (0.45 mmol, 1.5 equiv), NaI (1.2 mmol) were loaded in the glove box. Then the mixture was taken out of the box, degassed under vacuum, and back-filled with CO₂ gas for five times (each time lasted for 1 min). After that, anhydrous NMP (6 mL) was injected into the flask via a syringe and dissolved the mixture under the strong stirring until the mixture becoming transparent. Then two electrodes were submerged into the solution and conducted under 60 °C. Constant current (10 mA) was passed until the starting material was consumed. After electrolysis, the mixture was acidized by 2 N HCl solution (20 mL) and extracted by EtOAc for four times (30 mL × 4). The combined organic layers were washed with water (20 mL × 2) and brine (20 mL) and concentrated in vacuo. Then the residue was purified by silica gel column chromatography by using the petroleum ether/EtOAc to give out the carboxylic acid.

Fig. 6 Electrochemical and spectroscopic investigations. a CV tests of [Ni(acac)₂ + L] and LNi(acac)₂. Testing conditions: working electrode, glassy carbon electrode; counter electrode, Pt wire; reference electrode, Ag/AgNO₃ electrode (10 mM AgNO₃ in CH₃CN). Scan rate: 100 mV/s. Solvent: NMP/№Bu4NPF₆ (0.1 M). Samples were tested under N₂ atmosphere. Ni(acac)₂, 3 mM; L, dtbbpy, 3 mM, LNi(acac)₂, 3 mM. b UV-vis spectra of Ni(acac)₂, 3 × 10⁻⁵ M; L, 3 × 10⁻⁵ M; [Ni(acac)₂ + L], 3 × 10⁻⁵ M + 3 × 10⁻⁵ M and LNi(acac)₂, 3 × 10⁻⁵ M. NMP is chosen as the testing solvent. L = dtbbpy, 4,4′-di-tert-butyl-2,2′-bipyridine; NMP = 1-methyl-2-pyrrolidinone.

Fig. 7 Performance of nickel catalysts in CV tests. Testing conditions: working electrode, glassy carbon electrode; counter electrode, Pt wire; reference electrode, Ag/AgNO₃ electrode (10 mM AgNO₃ in CH₃CN). Scan rate: 100 mV/s. Solvent: NMP/№Bu4NPF₆ (0.1 M). Samples were tested under N₂ atmosphere except some cases under CO₂ atmosphere. a CV tests of [Ni(acac)₂ + dtbbpy] and aryl bromide 3h. Ni(acac)₂, 3 mM; L, dtbbpy, 3 mM; LNi(acac)₂, 3 mM; 3h, ethyl 4-bromobenzoate, 60 mM, CO₂ (bubbled in the solution for 10 min). b CV tests for the role of DMAP. [Ni], NiBr₂·DME, 3 mM; L, dtbbpy, 3 mM; LNi(acac)₂, 3 mM; 3b, 4-bromophenyl, 5 mM. c CV tests of adduct 1-1. adduct 1-1 (CO₂), 5 mM; CO₂ (bubbled in the solution for 10 min). L, dtbbpy, 4,4′-di-tert-butyl-2,2′-bipyridine; DMAP, 4-dimethylaminopyridine.
8. **Synthesis of 3a, 3c, 3e, 3h, 3m, and 3n (non-sacri
cial anode manner).** In an H-type divided cell equipped with a carbon felt cathode and a carbon felt anode in each chamber, aryl bromides (0.3 mmol), NiI2 (0.03 mmol, 10 mol%), 4,4′-di-tert-
butyl-2,2′-bipyrindine (0.03 mmol, 10 mol%), KO'Bu (0.15 mmol, 0.5 equiv), NaI (1.2 mmol) were loaded in the anodic chamber. In the anodic chamber, LiClO4 (1.2 mmol) was added. Then the reaction vial was taken out of the box, degassed under vacuum, and back-filled with CO2 gas for five times (each time lasted for 1 min). After that, anhydrous NMP (6 mL) was injected into each chamber via a syringe and dissolved the mixture under the strong stirring until the solution becoming transparent. Then dry Et3N (0.6 mmol) was injected into anodic chamber via syringe. After that, two electrodes were submerged into the solution. Constant cell voltage (3 V) was set to the reaction until the starting material was consumed at room temperature. After electrolysis, the mixture of both chambers was acidized by 2 N HCl solution (20 mL) and extracted by EtOAc for four times (30 mL × 4). The combined organic layers were washed with water (20 mL × 2) and saturated NH4Cl solution (20 mL) and concentrated in vacuo. Then the residue was purified by silica gel column chromatography by using petroleum ether/EtOAc to give out the carboxylic acids. Further details may be found in the Supplemental Information.

9. **Synthesis of 5b, 5c, and 5j (non-sacri
cial anode manner).** In a H-type divided cell equipped with a carbon felt cathode and a carbon felt anode in each chamber, alkyl halide (0.5 mmol), NiBr2-DME (0.05 mmol, 10 mol%), 6,6′-di-methyl-2,2′-
bipyrindine (0.1 mmol, 20 mol%), CsF (0.5 mmol, 1.0 equiv), LiClO4 (1.2 mmol) were loaded in the anodic chamber. In the anodic chamber, LiClO4 (1.2 mmol) was added. Then the reaction vial was taken out of the box, degassed under vacuum, and back-filled with CO2 gas for five times (each time lasted for 1 min). After that, anhydrous NMP (6 mL) was injected into each chamber via a syringe and dissolved the mixture under the strong stirring until the solution becoming transparent. Then dry Et3N (0.6 mmol) was injected into anodic chamber via syringe. After that, two electrodes were submerged into the solution. Constant cell voltage (3 V) was set to the reaction until the starting material was consumed at room temperature. After electrolysis, the mixture of both chambers was acidized by 2 N HCl solution (20 mL) and extracted by EtOAc for four times (30 mL × 4). The combined organic layers were washed with water (20 mL × 2) and saturated NH4Cl solution (20 mL) and concentrated in vacuo. Then the residue was purified by silica gel column chromatography by using petroleum ether/EtOAc to give out the carboxylic acids. Further details may be found in the Supplemental Information.

10. **Data availability**

The authors declare that the data supporting the findings of this study are available within the article and its Supplemental Information files. Extra data are available from the authors upon request.

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Competing interests
The authors declare the following competing financial interest(s): A Chinese Patent on this work has been authorized with the number (202010244592.7). The authors declare no other competing interests.

Additional information
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