Electrochemical cobalt-catalyzed selective carboxylation of benzyl halides with CO₂ enabled by low-coordinate cobalt electrocatalysts

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ABSTRACT: The direct, transition metal-catalyzed carboxylation of organohalides with carbon dioxide is a highly desirable transformation in organic synthesis as it utilizes feedstock chemicals and delivers carboxylic acids –among the most utilized class of organic molecules. Phenyl acetic acids, in particular, are privileged motifs that appear in many pharmaceuticals and biologically active compounds. This article reports the development of a sustainable and selective cobalt-catalyzed electrochemical carboxylation of benzyl halides with CO₂ to generate phenyl acetic acids. The success of this transformation is enabled by the development of low-coordinate cobalt/pyrox complexes as electrocatalysts to convert various benzyl chlorides and bromides to their corresponding phenyl/heteroaryl acetic acids with high selectivity over undesired homocoupling of the benzyl halides. The combination of electroanalytical methods, simulation studies, control reactions, and first-principles density functional theory (DFT) calculations informed the mechanistic analysis of this reaction. An EC'C-type activation mechanism of benzyl halides, which is unique to Co(II)/pyrox electrocatalysts, provides the rationalization of the exceptional observed selectivity for carboxylation. Specifically, the Co(II)/pyrox catalyst undergoes reduction to Co(I) followed by halogen abstraction and a favorable radical rebound to Co(II)/pyrox to form alkyl–Co(III) intermediates. Although voltammetry only shows a single electron transfer step, bulk electrolysis shows a two electron process and using DFT calculations, the intermediates are proposed to undergo two-electron reduction to alkyl–Co(I) followed by a ZnCl₂-assisted CO₂ insertion to form the carboxylated adducts with regeneration of Co(I)/pyrox.

1. INTRODUCTION

Metal-catalyzed carboxylation of organohalides and pseudohalides with CO₂ as the C1 source is a powerful approach for synthesizing carboxylic acids.¹ Traditionally, this is accomplished using highly reactive organomagnesium, lithium, or zinc reagents.² Unfortunately, the use of pyrophoric metal sources in stoichiometric amounts and the need for well-defined dialkylzinc reagents constitute significant drawbacks of these methods. Thus, the development of alternative methods that utilize more stable and readily available coupling partners without the use of sensitive organometallic reagents could provide an attractive solution for using CO₂ to form carboxylic acids.

In this context, major advancements in the catalytic carboxylation of organohalides using group 10 (Pd or Ni) catalysis have been reported (Fig. 1A)^{1,3–6} instigated by the initial work by Osakada and Yamamoto in 1994 on the direct carboxylation of organometallic nickel complex Ph–Ni(L)Br (L = bipyridine) with CO₂.⁷ Of particular interest, the first Ni-catalyzed carboxylation of benzyl halides with CO₂ was reported by Martin and

co-workers to produce phenyl acetic acids in good yields.⁵ This reaction type delivers phenyl acetic acids that are highly represented in carboxylic acid containing biologically relevant compounds. The groups of Yu and He reported an analogous carboxylation reaction utilizing Pd catalysis.⁶

In contrast to the use of group 10 metals, the use of less toxic and more sustainable transition metals such as cobalt have been far less developed for similar reactions (Fig. 1B).⁸ Sporadic examples of cobalt-catalyzed carboxylation reactions have been reported but only functional for specific organohalides.^{9–15} Perichon and co-workers presented the first cobalt catalyzed electrochemical carboxylation of benzyl halides using cobalt salen complexes which resulted in moderate yields of phenyl acetic acids.¹³ However, the practical synthetic utility of this method is hampered by several limitations due to the requirement of a Hg pool as the working electrode, high catalyst loading forcing reductive potentials, and the use of carcinogenic hexamethylphosphoramide (HMPA) as a co-solvent. More recently, Wang and Lu reported a cobalt-catalyzed carboxylation of benzyl halides using cobalt-salen catalyst with improvement

on the electrochemical reaction conditions.¹⁴ Using 1-chloroethyl benzene as the only benzyl halide example, the homocoupling of the benzyl halide was predominantly obtained as the major product, while the desired carboxylic acid was achieved in low yields. The unselective formation of the homocoupling product was presumed to be formed by the coupling of benzylic radicals generated after halogen abstraction from electrochemically generated high-coordinate Co(I)-salen complex.^{14,16} This observation constitutes one of the major challenges in developing electrochemical cobalt-catalyzed cross-coupling reactions of benzyl halides.¹⁶

To circumvent this undesirable process, we hypothesized that the discrete formation of an alkyl-cobalt intermediate via a radical rebound mechanism after the generation of the benzyl radical would capture the free benzylic radicals.^{17,18} The use of low-coordinate cobalt complexes was proposed in order to favor a radical rebound mechanism, although the use of such electrocatalysts is challenging due to rapid disproportionation of the electrochemically generated Co(I) complex.^{19,20} In this context, using an array of electroanalytical and physical organic

tools, our groups have found and investigated that electrochemically generated low-coordinate Co(I) complexes can be stabilized by electronically asymmetric *N,N*-pyrox ligands.¹⁹ These complexes are also competent electrocatalysts for the formal oxidative addition of benzyl bromides and chlorides.¹⁷

Leveraging the unique reactivity of the Co/pyrox system, and our on-going effort in the development of TM-catalyzed electrochemical cross-coupling reactions,²¹ we report herein a highly selective electrochemical cobalt-catalyzed cross-coupling reaction of benzyl halides with CO₂ to generate phenyl acetic acids. Combining electrochemical methods, experimental control reactions, and first-principles density functional theory (DFT) calculations, we provide insight into the reaction mechanism. Specifically, mechanistic studies were performed to probe the observed product selectivity in lieu of homocoupling, the propensity of radical rebound mechanism, and to elucidate the active cobalt species in radical rebound and carboxylation steps. Importantly, these insights into low-coordinate cobalt electrocatalysis provide foundational understanding of how cobalt electrocatalysts can be designed for selective carboxylation.

A. Pd- or Ni-catalyzed carboxylation

B. Co-catalyzed electrochemical carboxylation (this work)

C. Examples of biologically active phenyl acetic acids

D. Initial report on Co-catalyzed electrochemical carboxylation of benzyl halides

Perichon, **1985** (ref 13)

Wang and Lu, **2014** (ref 14)

- homocoupling of benzyl halide as predominant pathway
- very limited to specific example of alkyl halides/carboxylic acids
- requirement of Hg pool working electrode
- higher working potential, CO₂ pressure, or temperature

Figure 1. Transition metal-catalyzed carboxylation of activated and benzylic halides with CO₂ and examples of biologically active phenyl acetic acids.

2. RESULTS AND DISCUSSIONS

2.1 Development of a selective cobalt-catalyzed electrochemical carboxylation. Using conditions similar to those reported by Wang and Lu for cobalt salen (**A**) mediated electrocatalytic carboxylation,¹⁴ we examined the carboxylation reactions by utilizing low-coordinate cobalt electrocatalysts with various *N,N*-bidentate ligands. The electrocatalytic carboxylation of 1-chloroethylbenzene **1** with CO₂ was performed using 5 mol % cobalt electrocatalyst. The electrolyses were performed under a constant applied potential of −1.25 V at room temperature and ambient CO₂ pressure in a solution of tetrabutylammonium bromide (TBAB) in DMF (0.1 M) with Zn as a sacrificial anode. Results from representative examples are summarized in Fig. 2 (for details and examples of other *N,N*-bidentate ligands screened, see the SI).

Using the Co/bipyridine electrocatalyst (**B**), the desired product 2-phenylpropionic acid **2** was observed; however, in low yield and low product selectivity (vs homocoupling). The observed low yields and conversions to the desired carboxylic acid product can be attributed to the competing decomposition of the electrochemically reduced Co(I)/bipyridine complexes via the disproportionation reaction.¹⁹ We next investigated the carboxylation reaction under analogous conditions utilizing the Co electrocatalyst with *N,N*-pyrox ligands. All of the Co/pyrox electrocatalysts examined gave high yields (~90 % yield of **2**) with exceptional selectivities for the desired carboxylation product **2** in lieu of the homocoupling product. The influence of the anode material was also investigated. Sacrificial anodes such as Zn, Mg and Al were found highly effective, comparable to several reports on TM-catalyzed electrochemical carboxylation reactions.⁹ Non-sacrificial anodes such as RVC, carbon

felt, or platinum gave 0% or trace amount of carboxylic acid product (see SI for details). Other reaction parameters, such as solvent, electrolyte, and catalyst loading were also examined (see the SI for details). Overall, the conditions depicted in Fig. 2 using catalyst **C** were found to be optimal. With the commercial availability of the pyrox ligand shown in catalyst **C**, this electrocatalyst was utilized in subsequent investigations.

For comparison of a carboxylation reaction utilizing high-coordinate cobalt electrocatalysts, the electrolysis was performed using cobalt salen as the electrocatalyst (**A**) (Fig. 2). The reaction gave 13% yield of the desired carboxylic acid product (**2**) as well as the homocoupling byproduct (**3**) in 60% yield. Other unwanted byproducts such as ethyl benzene and styrene were also observed in minimal amounts.

Figure 2. Development of a selective cobalt-catalyzed electrochemical carboxylation reaction. Reaction conditions: 0.1 mmol benzyl chloride **1**, 5 mol % cobalt electrocatalyst in 0.1 M TBAB in DMF (4 mL) saturated with CO₂. Electrolysis was performed with applied potential of –1.25 V at room temperature for 16 h, using Zn rod as the anode and carbon felt as the cathode. Yields of **2** were based on ¹H NMR analysis and yields of **3** and other byproducts were based on GC analysis of the crude mixture using mesitylene as internal standard. See the Supporting Information for details.

2.2 Voltammetry and DFT studies to understand the activation step and product selectivity. In an effort to interrogate the significant differences in the observed selectivity for carboxylation versus homocoupling using different electrocatalysts, we examined the activation step involved in the reaction of benzyl chloride **1** with the requisite electrochemically generated Co(I) complex using cyclic voltammetry (CV). CVs were performed using 1 mM cobalt electrocatalyst in the absence (red voltammograms) and in the presence of benzyl chloride **1** (blue voltammograms) at a scan rate of 100 mV/s. The resulting voltammograms are summarized in Fig. 3A. Voltammograms shown for the cobalt electrocatalysts (red) in the absence of benzyl halide where designated as Co(II)/Co(I) redox couples.^{14,19} The addition of 1 equivalent of benzyl chloride **1** resulted in a significant change in the CV behavior for each electrocatalyst, denoting that in all systems, an EC-type mechanism (electron transfer, followed by a chemical reaction) is involved. More specifically all three cases showed a one-electron reduction of Co(II) to Co(I) is followed by a chemical reaction of the electrochemically reduced Co(I) complex with benzyl halide **1**. The chemical reaction involved is proposed to be a halogen atom abstraction to generate a benzyl radical and regenerate the Co(II) catalyst.¹⁷

However, the CV behaviors observed for each electrocatalyst in the presence of increasing concentrations of benzyl chloride **1** were notably different. For the cobalt salen complex

A, a catalytic current, denoted by the significant increase in peak current, was observed upon addition of **1** as well as with increasing concentration of **1**. This is typical CV behavior for an EC' mechanism (electron transfer, followed by a catalytic chemical reaction), where the chemical reaction regenerates the electroactive Co(II) catalyst. As such, this type of mechanism (one-electron reduction of Co(II) to Co(I), followed by halogen abstraction) predominantly generates benzyl radicals that can easily undergo dimerization via homocoupling to form **3** as the major product. Potential disproportionation reactions of the benzyl radical may account for the formation of minor amounts of the ethyl benzene and styrene byproducts shown in Figure 2.

The CV behavior observed with Co/bipyridine electrocatalyst also shows a catalytic current upon the addition of benzyl chloride **1**. However, the increase in the peak current is less significant upon addition of benzyl chloride **1**. This CV behavior is either indicative of an EC' mechanism with a slower catalytic activity or an EC'C type mechanism, wherein an EC' mechanism is operational but followed by another chemical reaction. Radical rebound mechanisms have been postulated to operate with low-coordinate cobalt complexes,¹⁷ and similar to those studies with low-coordinate nickel complexes,²² so we hypothesize the accompanying chemical reaction may be a radical rebound reaction of the benzyl radical to the Co(II)/bipyridine catalyst to generate a benzyl-Co(III) intermediate.

A. CV analysis for the activation of benzyl chloride **1 with cobalt electrocatalysts **A** to **C**.**

B. Mechanistic implications and rationale for product selectivity.

Figure 3. Mechanistic studies using cyclic voltammetry and implications to understand the activation step and product selectivity. (A, B) Understanding product selectivity and mode of activation by cyclic voltammetry. Conditions for CV analysis: 1.0 mM cobalt electrocatalyst with varied concentrations of benzyl chloride **1** in 0.1 M TBAPF₆ in acetonitrile (2.0 mL) at a scan rate of 100 mV/s. Electrochemical mechanisms were described as E for an electron transfer (one-electron reduction for this case), C for a chemical reaction, and C' for a catalytic chemical reaction. Currents in μA and potentials in V vs Fc⁺/Fc⁰. (See the Supporting Information for details).

Finally, the Co/pyrox electrocatalyst demonstrated the most distinct CV behavior. The addition of benzyl chloride **1** does not show a catalytic peak current. Moreover, the addition of increasing concentration of **1** showed a decrease in current as well as a shift in cathodic peak potential. This behavior is analogous to our previously reported mechanistic studies using CoBr₂ and related pyrox ligands with benzyl bromides, where an EC'C-type mechanism is proposed to be operational.¹⁷ Specifically, the accompanying chemical reaction (denoted as the second C) fully consumes the regenerated Co(II) catalyst via a faster radical rebound reaction versus that observed in Co/bipyridine. This proposed activation step is further supported by DFT studies (*vide infra*) and CV simulations. Overall, the highly favorable radical rebound mechanism that operates in Co/pyrox systems makes these electrocatalysts effective in generating the desired alkyl-cobalt intermediates and ultimately suppressing competing radical homo-coupling.

The CV behavior of catalyst C in the presence of benzyl chloride **1** was interrogated by fitting experimental voltammetry using a finite difference modeling package, as discussed in detail in the Supporting Information.²³ Briefly, experimental voltammograms were collected over multiple cy-

cles at a range of scan rates and benzyl chloride concentrations. Subsequently, kinetic and thermodynamic parameters associated with the proposed EC'C mechanism were adjusted to provide the fit presented in Figure 4A with the following parameters: $E^{0'} = -1.23$ V, $k^0 = 0.0035$ cm/s, $\alpha = 0.3$, $K_{\text{eq},1} = 1 \times 10^{20}$, $k_{f1} = 6 \text{ M}^{-1}\text{s}^{-1}$, $K_{\text{eq},2} = 4 \times 10^5$, $k_{f2} = 1 \times 10^5 \text{ M}^{-1}\text{s}^{-1}$ (see SI Table S1 for details). Importantly, this set of simulated parameters reproduces the key voltammetric feature observed in the experimental voltammetry (Fig. 4A), namely the decrease in both the cathodic and peak currents for catalyst C in presence of the benzyl chloride upon continuous voltammetric. The relatively good agreement between experimental and simulated voltammograms supports the proposed EC'C mechanism, in agreement with prior voltammetry reported by our group using analogous Co/pyrox system with benzyl bromide substrate.¹⁷ Additional details probing the concentration and scan rate dependence of experimental and simulated cyclic voltammograms are provided in the Supporting Information.

First-principles DFT calculations were carried out in parallel to examine the reaction energies and activation barriers for the proposed elementary steps. The calculations were performed using the Gaussian 16 software package,²⁴ with the M06-L exchange-correlation functional,²⁵ Stuttgart/Dresden

effective core potentials for Co and Zn atoms,²⁶ and 6-311++G(d,p) basis set for the rest of the atoms²⁷ (details in section VI(a) of the SI). DFT predicts that the Co(II)/pyrox electrocatalyst undergoes an initial one-electron reduction with calculated $E_0 = -1.41$ V (vs Fc^+/Fc^0)²⁸ to form the Co(I)/pyrox, comparable with the -1.23 V reduction potential from the voltammetry results. This initial reduction is followed by an exergonic halogen abstraction ($\Delta G = -16.0$ kcal/mol) by Co(I) with a low free energy barrier of $\Delta G^\ddagger = +1.4$ kcal/mol (see transition state structure **TSS** in Fig. 4B) to form the benzyl radical and regenerate the Co(II)/pyrox electrocatalyst. The benzyl radical can subsequently react via

a radical rebound mechanism on the Co(II)/pyrox complex to form an alkyl-Co(III) intermediate. DFT calculations suggest that the radical rebound on the Co(II)/pyrox complex is endergonic at $\Delta G = +9.9$ kcal/mol. These results are consistent with the initially proposed EC'C-type mechanism from the cyclic voltammetry studies. Based on the theoretical and experimental results, we propose that the second chemical reaction in the EC'C-type of activation of Co(II)/pyrox catalyst involves radical rebound on the electrochemically regenerated Co(II)/pyrox complex. Other possible spin states for the Co species were also examined but resulted in higher free energy requirements for all of the proposed elementary steps (see section VI(b & c) of SI for details).

A. Experimental and simulated CV for catalyst C with 0, 1, and 4 mM benzyl chloride 1.

B. DFT studies for the activation step using catalyst C: halogen abstraction and radical rebound

Figure 4. Mechanistic studies using experimental and simulated cyclic voltammetry and computational methods to rationalize an EC'C mechanism for catalyst **C** with benzyl chloride **1**. (A) Conditions for CV analysis: 1.0 mM cobalt electrocatalyst with varied concentrations of benzyl chloride **1** in 0.1 M TBAPF6 in acetonitrile (2.0 mL) at a scan rate of 100 mV/s. Currents in μA and potentials in V vs Fc^+/Fc^0 . Simulation parameters: $E^0 = -1.23$ V, $k^0 = 0.0035$ cm/s, $\alpha = 0.3$, $K_{\text{eq},1} = 1 \times 10^{20}$, $k_1 = 6 \text{ M}^{-1}\text{s}^{-1}$, $K_{\text{eq},2} = 4 \times 10^5$, $k_2 = 1 \times 10^5 \text{ M}^{-1}\text{s}^{-1}$. (B) DFT-calculated reactant, transition state, intermediate and product structures and the corresponding free energy profile for the halogen abstraction by Co(I) followed by radical rebound on Co(II) in the proposed EC'C mechanism. H atoms are omitted for clarity. The paranthesis show the most stable spin state for each intermediate, triplet (T). See the Supporting Information section VI (b & c) for details.

2.3 Mechanistic insights on carboxylation step. The carboxylation step for Pd and Ni-catalyzed carboxylations of organohalides has been studied and results from these reports have been valuable in the development of other catalytic reactions.

As such, we next evaluated the mechanism involved in the electrochemical cobalt-catalyzed carboxylation of the benzyl-cobalt intermediate (Fig. 5). This step can proceed either through the direct reaction of CO_2 with a benzyl-cobalt intermediate

(*path a*, Fig. 5A) or via the reaction of CO₂ with an *in situ* formed organozinc (or organomagnesium) reagent (*path b*). The traditional organometallic reagent can be formed via a one-electron electrochemical reduction of the benzyl radical to generate a carbanion²⁹ paired with a Zn²⁺ (or Mg²⁺) counter ion, or by the transmetalation of the benzyl-cobalt intermediate with Zn²⁺ (or Mg²⁺). The Zn²⁺ (or Mg²⁺) salts are generated from the sacrificial anode as denoted by the consumption of the Zn (or Mg) anode as the reaction progresses. To rule out *path b*, direct carboxylation reactions of benzylzinc chloride and benzylmagnesium chloride reagents with CO₂ in DMF were performed (Fig. 5B and 5C). The slow addition of benzylmagnesium chloride to a CO₂-saturated solution of 0.1 M TBAB in DMF at room temperature resulted in the exclusive formation of benzaldehyde. In the absence of CO₂, benzaldehyde was also observed as the only product as a result of benzylmagnesium reaction to DMF.³⁰ In addition, an analogous reaction using benzylzinc chloride resulted in the formation of toluene after acidic work-up.⁵ In both

cases, carboxylated phenyl acetic acid (**4**) was not observed. In addition, our DFT results show that the reduction potential for the one-electron reduction of the benzyl radical to the corresponding carbanion is -2.08 V (vs Fc⁺/Fc⁰), which is significantly more negative than the one electron reduction of the Co(II)/pyrox electrocatalyst ($E_0 = -1.41$ V (vs Fc⁺/Fc⁰)) (Fig. 5D), indicating that more negative cathodic potentials will be required to reduce the radical. A previous experimental study reported $E_{1/2} = -1.94$ V (vs Fc⁺/Fc⁰) for reducing the benzyl radical species, which agrees well with the calculated value.³¹ Overall, the experimental and theoretical results rule out carboxylation via *path b* and indicate that carboxylation does not involve the formation of benzyl zinc/magnesium halide intermediates.³²

A. Two possible carboxylation pathways

B. Reaction of benzyl Grignard reagent with CO₂ in DMF

C. Reaction of benzyl zinc reagent with CO₂ in DMF

D. Calculated one-electron reduction potentials of benzyl radical and alkyl-Co(II)/pyrox intermediates

E. DFT studies on the carboxylation step

Figure 5. Mechanistic investigation on the carboxylation step. (A) Possible pathways for the carboxylation step. (B, C) Reactions of benzylzinc and benzylmagnesium chloride reagents with CO₂ in DMF. (D) Calculated E_0 values for reduction of benzyl radical and alkyl-Co(III) intermediates. (E) DFT-calculated reactant, transition state, intermediate and product structures along with the corresponding free energy profiles for the carboxylation of (a) alkyl-Co(II), (b) alkyl-Co(I), and (c) ZnCl₂-assisted alkyl-Co(I) intermediates with CO₂. H atoms are omitted for clarity. The parenthesis show the most stable spin state for each intermediate, triplet (T) and quartet (Q). See the Supporting Information for detailed experimental and computational details.

DFT studies further probed the feasibility of the carboxylation step via *path a*. Several key features of the mechanism associated with the carboxylation step were examined. These include, the nature of the cobalt species involved in carrying out

the carboxylation, the feasibility of an inner-sphere CO₂ insertion, and the involvement of Zn²⁺ (or Mg²⁺) ions on the carboxylation step (Fig. 5E). We initially examined the nature of the alkyl-cobalt intermediate that is active in the carboxylation with CO₂. Carboxylation can proceed either via (Fig. 5E(a)) the

insertion of CO₂ into the alkyl–Co(II) bond, with alkyl–Co(II) formed after radical rebound in oxidative addition and subsequent one-electron reduction of alkyl–Co(III), or (Fig. 5E(b)) via insertion into an alkyl–Co(I) bond that forms via a one-electron reduction of the alkyl–Co(II) intermediate. The two-electron reduction potentials were calculated to be $E_0 = -0.63$ and -1.47 V (vs. Fc^+/Fc^0) (Fig. 5D). An inner-sphere CO₂ insertion to both the alkyl–Co(II) and alkyl–Co(I) intermediates were calculated to be exergonic at $\Delta G = -12.3$ and -13.2 kcal/mol, respectively. However, the CO₂ insertion at the alkyl–Co(II) resulted in a very high free energy of activation at $\Delta G^\ddagger = +25.8$ kcal/mol (TSS in Fig. 5E(a)). In contrast, CO₂ insertion into the alkyl–Co(I) intermediate was found to initially involve an endergonic CO₂ binding on the cobalt(I) center at $\Delta G = +12.1$ kcal/mol, followed by an inner-sphere CO₂ insertion step with an overall free energy barrier at $\Delta G^\ddagger = +21.2$ kcal/mol (TSS in Fig. 5E(b)). The activation barrier is 4.6 kcal/mol lower for the alkyl–Co(I) intermediate ($\Delta G^\ddagger = 21.2$ kcal/mol) compared to the alkyl–Co(II) intermediate ($\Delta G^\ddagger = 25.8$ kcal/mol). The reduced barrier can be attributed to the presence of a vacant site and increased electron density on the Co atom in the alkyl–Co(I) intermediate than the alkyl–Co(II) intermediate. While the alkyl–Co(II) intermediate is a d^7 15 e^- complex, the alkyl–Co(I) intermediate is a d^8 14 e^- complex and has a higher d electron count. The lower barrier of the alkyl–Co(I) intermediate than the alkyl–Co(II) intermediate and the facile reduction potential of the alkyl–Co(II) intermediate with $E_0 = -1.47$ V (vs. Fc^+/Fc^0) suggests that the alkyl–Co(I) intermediate is likely the active species for carboxylation. Outer-sphere CO₂ insertion mechanisms were also investigated but they led to endergonic product energies (see section VI(d) of the SI). As such, we propose a carboxylation step that proceeds via *path a* involving an inner-sphere CO₂ insertion into the alkyl–Co(I) intermediate. This proposal is analogous to the recently reported CO₂ insertion mechanism by Martin and coworkers on isolated alkyl–Ni(I)/L (L = phenanthroline) complexes using detailed experimental and DFT studies.³³

We next carried out calculations to examine the carboxylation step in the presence of a Lewis acid salt derived from the sacrificial anode (Fig. 5E(c)). The Lewis acid Zn^{2+} readily coordinates with the electron rich oxygen on the CO₂ to stabilize the electron transfer from the Co(I)-alkyl complex into the CO₂. Using ZnCl_2 as the Lewis acid, the carboxylation on alkyl–Co(I) intermediate was found to be highly exergonic at $\Delta G = -25.1$ kcal/mol (compared to -13.2 kcal/mol without ZnCl_2) with a low free energy of activation at $\Delta G^\ddagger = +14.1$ kcal/mol (TSS in Fig. 5E(c)) (compared to $+21.2$ kcal/mol without ZnCl_2). The Lewis acidity of the salts facilitates electron transfer from the oxygen to the metal cation, thus increasing the electrophilicity of CO₂, which aids in the reaction at the Co atom. This is very similar to proton-assisted electron transfer and activation of CO₂ in the electrocatalytic reduction of CO₂ over group 11 and post transition metal electrodes³⁴ and in [NiFe]CO dehydrogenase.³⁵ The final metathesis step regenerates the Co(I)/pyrox catalyst and releases the carboxylate adduct. The carboxylation step is facilitated by the sacrificial anodes, which is consistent with experimental results that show that non-sacrificial anodes result in only trace formation of the carboxylic product. The use of MgCl_2 as a Lewis acid showed very similar results, including two plausible conformations of the salt's interaction with CO₂ (see section VI(d) of the SI). These results are analogous to the

previously reported DFT calculations on Lewis acid-assisted carboxylation steps in Pd- and Ni-complexes.^{6,36}

2.4 Current mechanistic understanding. Based on the mechanistic studies detailed above, we propose the mechanism summarized in Fig. 6 to be a reasonable option. Other plausible mechanistic pathways are discussed in the SI Section VII. First, an EC'C-type activation mechanism step occurs via: (a) initial reduction of Co(II)/pyrox electrocatalyst to the Co(I)/pyrox intermediate followed by (b) halogen abstraction of benzyl chloride to generate a transient benzyl radical and regenerate the Co(II) electrocatalyst. The benzyl radical undergoes a favorable (c) radical rebound mechanism to Co(II)/pyrox complex forming an alkyl–Co(III)/pyrox intermediate. Based on the DFT calculations, the alkyl–Co(III)/pyrox intermediate is proposed to undergo an EEC-type carboxylation step which involves (d) an initial two-electron reduction of an alkyl–Co(III)/pyrox to an alkyl–Co(I)/pyrox intermediate. Then, reduction would be followed by a (e) ZnCl_2 -assisted inner-sphere CO₂ (see Fig. 5E) insertion to the alkyl–Co(I)/pyrox intermediate to form the carboxylated adduct. Metathesis (f) with the Zn^{2+} (or Mg^{2+} if Mg is used as the anode) from the oxidation of the sacrificial anode would lead to the formation of the desired carboxylic acid product (following acid work-up) and regeneration of the active Co(I) electrocatalyst. This mechanism is consistent with a one electron activation of the electrocatalyst and two electron production of the product observed via bulk electrolysis. However, we did not distinctly observe these two-electron reduction steps in the CV studies, possibly due to the reactive nature of the alkyl–Co(III) intermediate whose first electron reduction will be very rapid at the operating cathodic potential. As such, we believe that future mechanistic work in this area needs further study to understand this complex system.

A potential alternative mechanism can be proposed (see SI, Fig. S17) where CO₂ insertion on R–Co(II) intermediate happens rather than R–Co(I). Experimental evidence, however, partially disproves this alternative step. First, the reaction of benzyl magnesium bromide with stoichiometric amount of Co(II)/pyrox to generate R–Co(II)/pyrox in the presence of CO₂ did not lead to the formation of the carboxylic acid product (Figure 5B). Second, when CV studies were performed in the presence of CO₂ (SI, Fig. S19) as well as in the presence of Zn^{2+} (SI, Fig. S20), no evidence of the regeneration of Co(II)/pyrox complex were observed, which would be expected if CO₂ insertion happens on the R–Co(II) intermediate. Additional alternative mechanism is also presented and discussed in the SI (Fig S18).

Additional control experiment was also carried out by performing the electrolysis in undivided cell using Pt counter electrode in the presence and absence of ZnCl_2 (1 equiv.) as additive. Only trace product was observed in the absence of ZnCl_2 while 78% yield of the desired carboxylated product was obtained in the presence of ZnCl_2 using Pt as the counter electrode. This suggests that the sacrificial anode (in its oxidized form, i.e. Zn^{2+}) is critical for the carboxylation reaction and regeneration of the catalyst. The presence of Zn^{2+} or Mg^{2+} were also found essential in related non-electrochemical Pd and Ni-catalyzed carboxylation reaction reactions.^{5,6} Recently, MgBr_2 as an inorganic salt was employed in an electrocarboxylation reaction, showing that use of these salts in an undivided cell can lead to more sustainable process eliminating the use of sacrificial anode, but further asserting the essential role of the salts in the carboxylation reaction.³⁷

Figure 6. Proposed mechanism for the cobalt-catalyzed carboxylation of benzyl halides with CO_2 and Co/pyrox electrocatalyst C. Electrocatalyst Co(II)/pyrox undergoes (a) one-electron reduction to generate Co(I) complex that activates benzyl halides via (b) halogen abstraction. (c) Radical rebound of the benzyl radical to C generates the R-Co(III) intermediate. Two-electron reduction (d) of this intermediate to R-Co(I) followed by (e) CO_2 insertion then (f) transmetalation with ZnCl_2 (generated at the anode) gives the carboxylate product and regenerates the Co(I) active catalyst. For alternative proposed mechanisms, see the SI Section VII.

2.5 Substrate scope and limitations. We next investigated the scope of the reaction by performing electrochemical carboxylations with various organohalides (Fig. 7).³⁸ Primary benzyl chlorides and bromides with electronically different substituents and functional groups on the arene ring gave high yields of the desired carboxylic acid products. Specifically, benzyl halides containing ethers, nitriles, esters, and halides (fluorine, chlorine) were tolerated and gave phenyl acetic acids (**4–14**) in high yields. Ortho-substituted benzyl halides were also converted to carboxylic acids (**10–14**). Several secondary benzyl chlorides and bromides were also converted to secondary phenyl acetic acids in good yields and selectivities (**2, 15–19, 24–25**). Carboxylic acid drugs such as ibuprofen (**24**) and naproxen (**25**) were obtained using this method in excellent yields.

Heterocycle-containing benzyl halides such as indole (**20**), benzofuran (**21**), pyrazole, (**22**), and dihydrobenzodioxine (**23**), were also converted to corresponding carboxylic acids. Notably, the utility of cobalt-salen **A** as the electrocatalyst conducted in selected substrates gave carboxylic acid products (**4,**

2, 25) in very low yields. Under these conditions, the homocoupling of the benzyl halides were observed as major products.

Several limitations of the current optimized method are summarized, and representative examples are shown in Fig. 7D. Tertiary benzyl halides and allylic halides gave low to trace amounts of the carboxylic acid product. In these cases, the homocoupling byproducts were observed as determined by GC-MS analysis of the reaction crude mixture. These can be rationalized by the slow or less favorable radical rebound of the highly stabilized radicals to Co(II)/pyrox complex.¹⁷ Aryl bromides and chlorides are also incompatible to the present carboxylation method giving only traces of aryl carboxylic acids. In this case, the oxidative addition (or halogen abstraction) of electrochemically generated Co(I)/pyrox catalyst to the aryl halides was found prohibitively slow in comparison to the rate of Co(I) disproportionation. In these cases, the starting aryl halide materials were recovered.

Figure 7. Scope of the carboxylation reaction and limitations. General reaction conditions: 0.5 mmol benzyl halide, catalyst **C** (5 mol % CoCl_2 , 5 mol % pyrox ligand), 0.1 M TBAB in DMF (9 mL) saturated with CO_2 . Electrolysis were performed with applied potential of -1.25 V at room temperature for 16 to 20 h, using Zn rod as anode and carbon felt as cathode. Isolated yields after column chromatography. Yields in parenthesis were based on ^1H NMR analysis of the crude. ^aReactions using cobalt salen as the catalyst. ^bReaction performed using controlled potential electrolysis at -1.0 V vs Ag wire. See the Supporting Information for details.

3. SUMMARY

In summary, the first general and selective cobalt-catalyzed electrochemical carboxylation of benzyl halides with CO_2 was developed. The selective carboxylation (over homocoupling of benzyl halides) was enabled by the use of Co/pyrox electrocatalysts to convert a variety of benzyl chlorides and bromides to phenyl/heteroaryl acetic acids at room temperature in high yields. Electroanalytical methods and DFT studies were utilized to help provide important mechanistic information for this transformation. Importantly, the exceptional selectivity observed was rationalized by an EC'C-type activation mechanism of benzyl halides that was found to be unique to Co(II) /pyrox electrocatalysts (over other types of cobalt electrocatalysts).

Specifically, the activation step involves the initial reduction of Co(II) /pyrox catalyst to Co(I) that activates benzyl halides via a halogen abstraction and a favorable radical rebound to Co(II) /pyrox to form alkyl- Co(III) intermediates. DFT calculations suggest that these intermediates are capable of undergoing an EEC-type carboxylation reaction, involving initial reduction to alkyl- Co(I) intermediates, followed by a favorable ZnCl_2 -assisted CO_2 insertion to form the carboxylated adducts. However, additional electron transfer steps are not observed voltammetrically, so future mechanistic studies are needed, but this work shows that low-coordinate cobalt electrocatalysts have potential for selective carboxylation.

ASSOCIATED CONTENT

Supporting Information

The Supporting Information is available free of charge on the ACS Publications website.

Experimental details, cyclic voltammograms, ^1H and ^{13}C NMR data of products, and DFT studies (PDF)

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Notes

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ABBREVIATIONS

pyrox, pyridine-oxazoline ligands; TBAB, tetrabutylammonium bromide; TBAPF₆, tetrabutylammonium hexafluorophosphate

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