Electroreductive Cobalt-Catalyzed Carboxylation: Cross-Electrophile Electrocoupling with Atmospheric CO₂

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Abstract: The chemical use of CO₂ as an inexpensive, nontoxic C1 synthon is of utmost topical interest in the context of carbon capture and utilization (CCU). We present the merger of cobalt catalysis and electrochemical synthesis for mild catalytic carboxylations of allylic chlorides with CO₂. Styrlylactic acid derivatives were obtained with moderate to good yields and good functional group tolerance. The thus-obtained products are useful as versatile synthons of γ-arylbutyrolactones. Cyclic voltammetry and in operando kinetic analysis were performed to provide mechanistic insights into the electrocatalytic carboxylation with CO₂.

The surge in the levels of carbon dioxide in the atmosphere nowadays is caused mainly by the industrialization of raw material production. As a major component of greenhouse gases, CO₂ contributes to global climate change with the increase in atmospheric temperature.[1] However, CO₂ can be used as an excellent C1 synthon/building block[2] for molecular syntheses and one successful utilization is the catalytic production of polycarbonates and cyclic carbonates from epoxides.[3] Carboxylation reactions are particularly desirable due to the formation of kinetically stable C–C bonds.[4] Cross-electrophile reactions have emerged as a powerful alternative for the formation of C–C bonds explicitly from electrophiles, providing an improvement in step economy.[5] Since CO₂ is thermodynamically stable and kinetically inert with a high activation barrier, its use as an inert electrophile mostly requires highly reactive nucleophiles, such as high-energy Grignard reagents.[6] The use of metal catalysts has favored such transformations by lowering the activation energy needed.[7] In the past, precious metals, such as palladium and rhodium, have dominated the field of carboxylation.[8]

However, recently, 3d transition metals have gained major momentum and are sought after due to their abundance and lower toxicity.[8,9] Notable examples of both precious and 3d transition metal catalysis include Satos’ studies on palladium-catalyzed carboxylations of allylic chlorides, and cobalt-catalyzed allylic C(sp³)–H carboxylation with CO₂, respectively.[10] Yet, both transformations used strong reducing agents, such as ZnEt₂ and AlMe₃. Similarly, Mei and Martin independently realized a nickel-catalyzed carboxylation of allylic alcohols using super-stoichiometric amounts of manganese or zinc powder as the reducing agent.[11] Electrocatalysis with 3d metal catalysts[12] has emerged as a powerful tool for sustainable molecular syntheses.[13] Recent advances for electrocarboxylation[14] include elegant palladium-catalyzed reductive transformations of allyl esters to useful carboxylic acids as reported by Mei (Scheme 1a).[15] Precedence includes the work of Perichon (Scheme 1),[16] who reported the electrocarboxylation of cinnamyl chloride with the use of a Hg pool cathode and a Co(salen) complex.[16] In addition to the effective usage of electrochemistry for the reductive carboxylation, it is intriguing to unravel effective 3d metal catalysts for the carboxylation reactions that are environmentally friendly. Herein, we report on a cobalt-catalyzed carboxylation of allylic chlorides with CO₂, featuring electricity as the sole reducing agent to access styrlylactic acid derivatives (Scheme 1b) as they are particularly useful as key synthons of numerous γ-arylbutyrolactones, which are structural motifs found in various natural products.[17]

We initiated our studies by optimizing the reaction conditions (Table 1) of the envisioned electrocarboxylation. Different cobalt salts were used as precatalysts with cinnamyl chloride 1a as the substrate. In particular, Co(salen) did not perform well, even at a higher loading of 10 mol% (entry 5).

Scheme 1. Cobalt-catalyzed electroreductive carboxylation.
Simple Co(OAc)_2 gave the best result, alongside CoCl_2 which gave a slight decrease in yield (see the Supporting Information). Control experiments verified the important role of electricity and the cobalt precatalyst (entries 3 and 4). The reaction was performed under constant current electrolysis, the required amount of current to provide full conversion of the starting material was found to be 10 mA for 6 hours with a Faradaic yield of 13 %. Notably, no reaction was observed without current. We found that polar aprotic solvents, such as DMF and DMSO, performed well for the direct carboxylation, however, differed, as DMF and DMSO, performed well for the direct carboxylation.\[^{[32]}\] Alternative ligands were explored, including bidentate nitrogen-containing ligands, such as bipyridine and 1,10-phenanthroline, but they performed poorly (entries 6 and 7).\[^{[19]}\] Instead, cost-effective triphenylphosphine ligands gave yields of the carboxylated products \[^{[c]}\] given in parentheses. \[^{[c]}\] 2 h reaction time.

With the optimized reaction conditions in hand, we explored the substrate scope of the cobalta-electrocarboxylation reaction (Scheme 2). Alkyl substituents in the ortho or para position of the cinnamyl chlorides \(^{[1b-d]}\) were well accepted to furnish the products \(^{[2b-d]}\) in addition, substrates containing para-substituted phenyl groups such as \(^{[2e]}\) and polycyclic rings such as anthracene \(^{[2f]}\) gave moderate yield, with higher branched selectivity. Electron-donating groups, such as benzo[dioxole \(^{[2g]}\), thioether \(^{[2h]}\), thioether \(^{[2i]}\), and methoxy \(^{[2l]}\), were well tolerated in this reaction. The regioselectivity, however, differed, as \(^{[2h]}\) provided more of the branched product, while substrate \(^{[2i]}\) reacted with higher preference for the linear product. Substrates with electron-withdrawing substituents, such as trifluoromethyl \(^{[2j]}\), resulted in good yield, with improved regioselectivity for the branched product. Halogen-containing substrates \(^{[1k-m]}\) resulted in good yields of the carboxylated products \(^{[2k-m]}\), with fluoro \(^{[2k]}\) and chloro \(^{[2l]}\) analogues giving higher selectivity for the linear product. The product \(^{[2n]}\) gave an indication that halogens are tolerated only to a certain extent as 5–10 % of the product was dehalogenated, giving rise to a small amount of \(^{[2a]}\) in the product mixture. This was explicitly shown when the para-iodo-containing substrate was tested and the dehalogenated product was isolated in 40 % yield. Under otherwise identical reaction conditions, the use of alkyl-substituted and heterocycle-substituted substrates has provided unsatisfactory results to date.\[^{[33]}\]

To better understand the catalyst mode of action, DFT calculations were carried out at the PW6B95-D4/def2-TZVPP + SMD(DMF)/TPSS-D3(BJ)/def2-SVP level of theory (Figure 1).\[^{[34]}\] The isomerization of the \(\eta^1\)-allyl complex to the \(\eta^2\)-allyl complex was revealed not to be the rate-determining step due to the low energy barrier of

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**Table 1:** Optimization of cobalt-catalyzed electroreductive carboxylation.\[^{[a]}\]

| Entry | Deviation from standard conditions | Yield[b] |
|-------|------------------------------------|---------|
| 1     | –                                  | 59 % (1:1) |
| 2     | CCE = 5 mA                         | 42 % (1:1) |
| 3     | no current                         | –       |
| 4     | without catalyst for 16 h          | 13 % (1:1) |
| 5     | Co(salen) (5 mol %)                | 27 % (1:1) |
| 6     | dppe instead of PPh_3              | 27 % (1:1) |
| 7     | bipyridine instead of PPh_3        | 8 % (1:2)  |
| 8     | 0.1 mol/L of 1a                    | 44 % (1:1) |
| 9     | Pt cathode                         | 35 % (1:1) |
| 10    | Fe anode                           | 37 % (1:1) |
| 11    | Cu anode                           | 10 % (1:1) |
| 12    | Zn anode                           | 38 % (1:1) |
| 13    | Mn reductant, no electricity       | traces   |
| 14    | Zn reductant, no electricity       | –       |
| 15    | T = 60 °C                          | 42 % (1:1) |
| 16    | CoCl(PPh_3)_3                      | 58 % (1:1) |

[a] Undivided cell, \(^{[1a]}\) (0.25 mmol), cobalt(II) acetate (10 mol %), PPh_3 (20 mol %), electrolyte (1.0 equiv), solvent (5.0 mL), 25 °C, 6 h, Mg foil electrode (3.0 mm × 15 mm × 0.2 mm), Ni foam electrode (10 mm × 15 mm × 1.0 mm), constant current electrolysis (CCE) at 10 mA. \[^{[b]}\] Yield of isolated product. Regioselectivity \(^{[2a,2a^\prime]}\) given in parentheses. \[^{[c]}\] 2 h reaction time.
16.1 kcal mol\(^{-1}\) for product 21. Given that the electrocatalysis of the cross-electrophiles was performed at relatively high current and high CO\(_2\) partial pressure, we directed our focus to the formation of the allylic C–C bond. The latter is preferred for the chlorinated substrate over the brominated substrate by 1.5 kcal mol\(^{-1}\). Therefore, the DFT studies have been shown to be in agreement with the experimentally observed regioselectivity of the product 21.

In order to understand the mechanism of this cobaltealectrocatalyzed carboxylation reaction with CO\(_2\), we sought to investigate the mode of action. First, we elucidated the kinetic profile (Figure 2a) of the standard reaction conditions together with the different simple cobalt salts as precatalysts for comparison in terms of the reaction rate. An in operando infrared spectroscopy (IR) method was adopted in this case. To our delight, simple Co(OAc)\(_2\) and the halide salts performed in a superior fashion (Figure 2b); a higher catalytic loading of Co(salen) was tried, but it did not improve the yield.\([20]\) Second, the preformed reduced cobalt(I) intermediate was of interest as this might indicate whether it is involved in the rate-determining step of this particular system. One such low-valent cobalt(I) intermediate has been reported for use in the amination reaction of unactivated aryl iodides\([21]\) and also in C–H activation reactions\([22]\).

**Figure 1.** Computed relative Gibbs free energies in kcal mol\(^{-1}\) for the a) isomerization of the \(\eta^1\)-allyl complex to the \(\eta^1\)-allyl form, and b) allylic C–C bond formation at the PW6B95-D4/def2-TZVPP + SMD (DMF)///TPSS-D3(BJ)/def2-SVP level of theory. Hydrogen atoms in the computed transition state structures were omitted for clarity.

**Figure 2.** a) Kinetic profile with 3D surface plot. b) Comparison of various cobalt catalysts.
Detailed mechanistic studies performed by means of cyclic voltammetry revealed that simple cobalt(II) complexes did not interact with the allylic chloride 1a (Figure 3a). The reduction potential of the parent cinnamyl chloride 1a was shown to be irreversible at $E = -1.90 \, \text{V vs. SCE}$. Interestingly, the cobalt(I) complex 3 showed one irreversible reduction peak at $E = -1.82 \, \text{V vs. SCE}$ (Figure 3b), which could correspond to the reduction of cobalt(I) to cobalt(0).[23] However, the addition of substrate 1a resulted in an oxidative addition of the substrate onto the cobalt(I) complex 3 to give a cobalt(III) intermediate. This could be seen as there are two reduction peaks and they could be plausibly assigned as $E = -1.70 \, \text{V vs. SCE}$ for the reduction of cobalt(II) to cobalt(I) and $E = -1.95 \, \text{V vs. SCE}$ for the reduction of cobalt(I) to cobalt(0) (Figure 3b).[24] The reduction of cobalt(III) to cobalt(II) was not observed as it has a much higher potential, usually in the positive range.[25] These results indicate that the oxidative addition of the substrate onto the active cobalt catalyst is possibly not involved in the rate-determining step. Stoichiometric reactions were also conducted with complex 3 without supply of electricity to rule out the possibility of in situ formed cobalt(III) being in the CO$_2$ activation step. Thus, the cathodic reduction of cobalt(III) intermediate to cobalt(I) is required to facilitate the formation of the carboxylated product.

A plausible catalytic cycle is proposed based on the obtained results (Scheme 3).[26] Initially, coordination of the alkene 1a onto the active cobalt(I) catalyst occurs. This, then, promotes the cleavage of the adjacent allylic C–H bond, resulting in an oxidative addition of substrate 1a to form an $\eta^1$-allyl-cobalt(III) intermediate II. At this stage, the intermediate II could undergo rearrangement to form the $\eta^1$-allyl-cobalt(III) intermediates III-A and III-B depending on different ligand effects. For instance, ligands containing heteroatoms such as O atoms are known to promote the tautomerization of $\eta^3$- to $\eta^1$-allyl intermediates in related cobalt complexes.[10a] There are two possible pathways from intermediates III, they can both undergo cathodic reductions to give the corresponding low-valent $\eta^1$-allyl-cobalt(I) species IV, which could be stabilized by an alkenyl or aryl ligand.[27] This determines the regioselectivity of the product which is highly dependent on the ligand employed. Here, the linear product is generated through C–C bond formation with CO$_2$ at the $\gamma$-position[28] to form the carboxylated product 2 and 2'.

In summary, we have developed an effective cobalt phosphine catalyst for the cross-electrophile electrocoupling of allylic chlorides without the use of harsh chemical reductants. In operando IR spectroscopy and cyclic voltammetry provided detailed insight into the reaction mechanism.

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Conflict of interest

The authors declare no conflict of interest.

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[26] For an alternative catalytic pathway, please see the Supporting Information.

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