Electrocatalysis

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. Styrylacetic 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, CO_2 contributes to global climate change with the increase in atmospheric temperature.[1] However, CO_2 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 CO_2 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.[8b, 9] Notable examples of both precious and 3d transition metal catalysis include Satos' studies on palladium-catalyzed carboxylations of allylic alcohols, and cobalt-catalyzed allylic C(sp³)−H carboxylation with CO_2, respectively.[10] Yet, both transformations used strong reducing agents, such as $ZnEt_2$ and $AlMe_3$. 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 cinammyl chloride with the use of a Hg pool cathode and a Co(salen) complex.[16e] 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 CO_2, featuring electricity as the sole reducing agent to access styrylacetic 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).
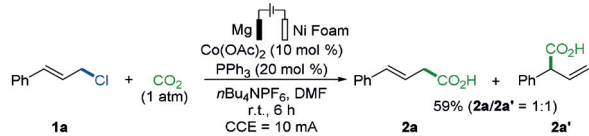
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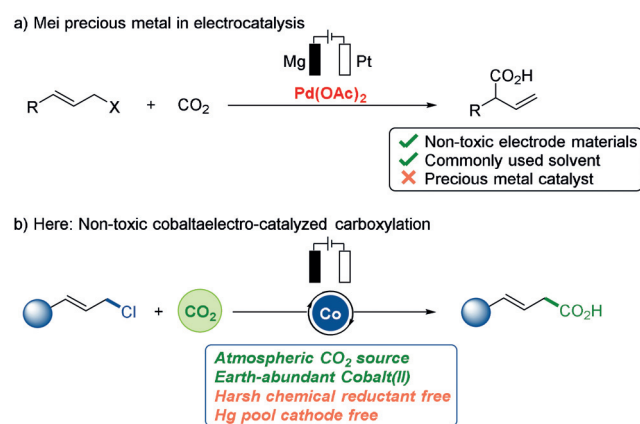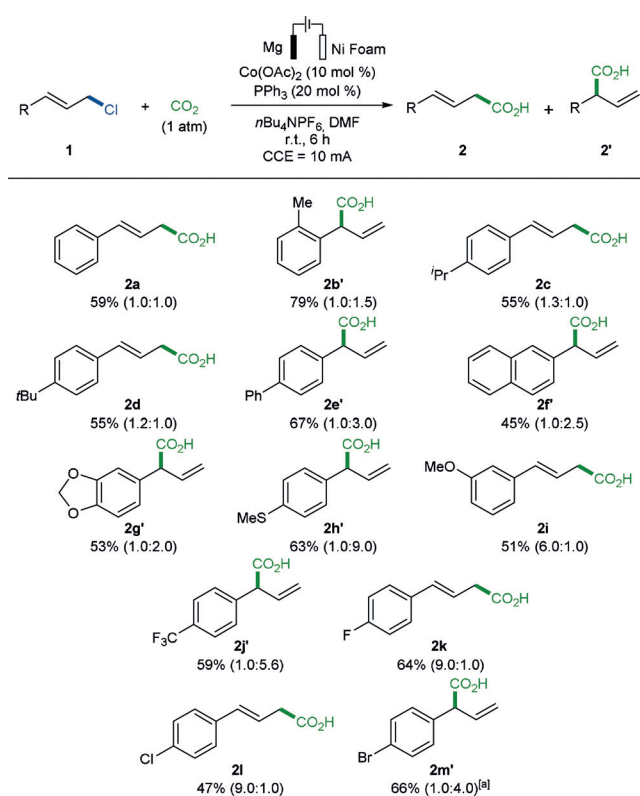
Scheme 1. Cobalt-catalyzed electroreductive carboxylation.

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 PPh₃	27% (1:1)
7	bipyridine instead of PPh₃	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(PPh₃)₃ **3**[c]	58% (1:1)

[a] Undivided cell, **1a** (0.25 mmol), cobalt(II) acetate (10 mol%), PPh₃ (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'** given in parentheses. [c] 2 h reaction time.

Simple Co(OAc)₂ gave the best result, alongside CoCl₂ 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.[18] 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 the best results. Different electrodes were next probed for both the cathode and the anode (entries 9–12). The platinum cathode gave lower yield than nickel foam as the cathode choice. Even though a few different anodes were tried, magnesium proved to be useful in decreasing the high overpotential for the carboxylation to occur. Moreover, the reaction was also performed with chemical reductants, such as manganese and zinc, but to no avail even at elevated temperature (entries 13 and 14).[19]

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

Scheme 2. Cobalt-catalyzed electroreductive carboxylation of cinnamyl chlorides **1** with CO₂. Regioselectivity **2/2'** given in parentheses, only major products are shown. [a] A mixture with 5% dehalogenated product **2m**.

polycyclic rings such as anthracene **2f'** gave moderate yield, with higher branched selectivity. Electron-donating groups, such as benzodioxole (**2g'**), thioether (**2h'**), and methoxy (**2i**), 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 **2m'** 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.[19]

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).[19] The isomerization of the η³-allyl complex to the η¹-allyl complex was revealed not to be the rate-determining step due to the low energy barrier of
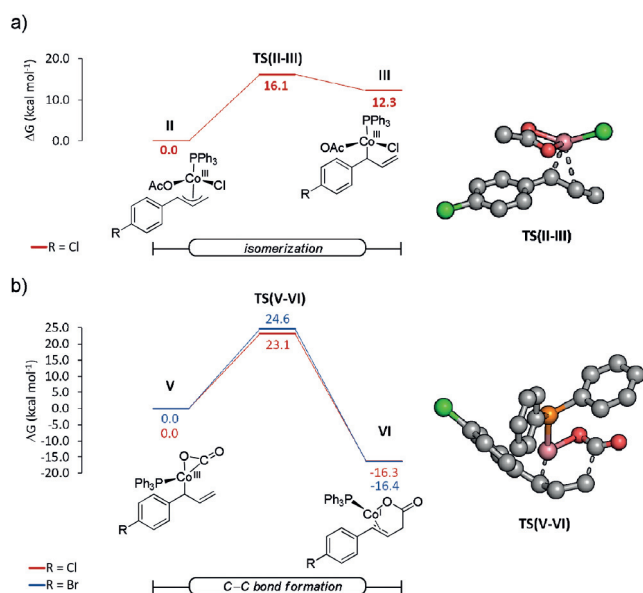
Figure 1. Computed relative Gibbs free energies in kcal mol^{-1} for the a) isomerization of the η^3-allyl complex to the η^1-allyl form, and b) allylic C−C bond formation at the PW6B95-D4/def2-TZVPP+SMD (DMF)//TPSS-D3(BJ)/def2-SVP level of theory. Hydrogen atoms in the computed transition state structures were omitted for clarity.

16.1 kcal mol^{-1} for product **2l**. 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 **2l**.

In order to understand the mechanism of this cobalta-electrocatalyzed 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]
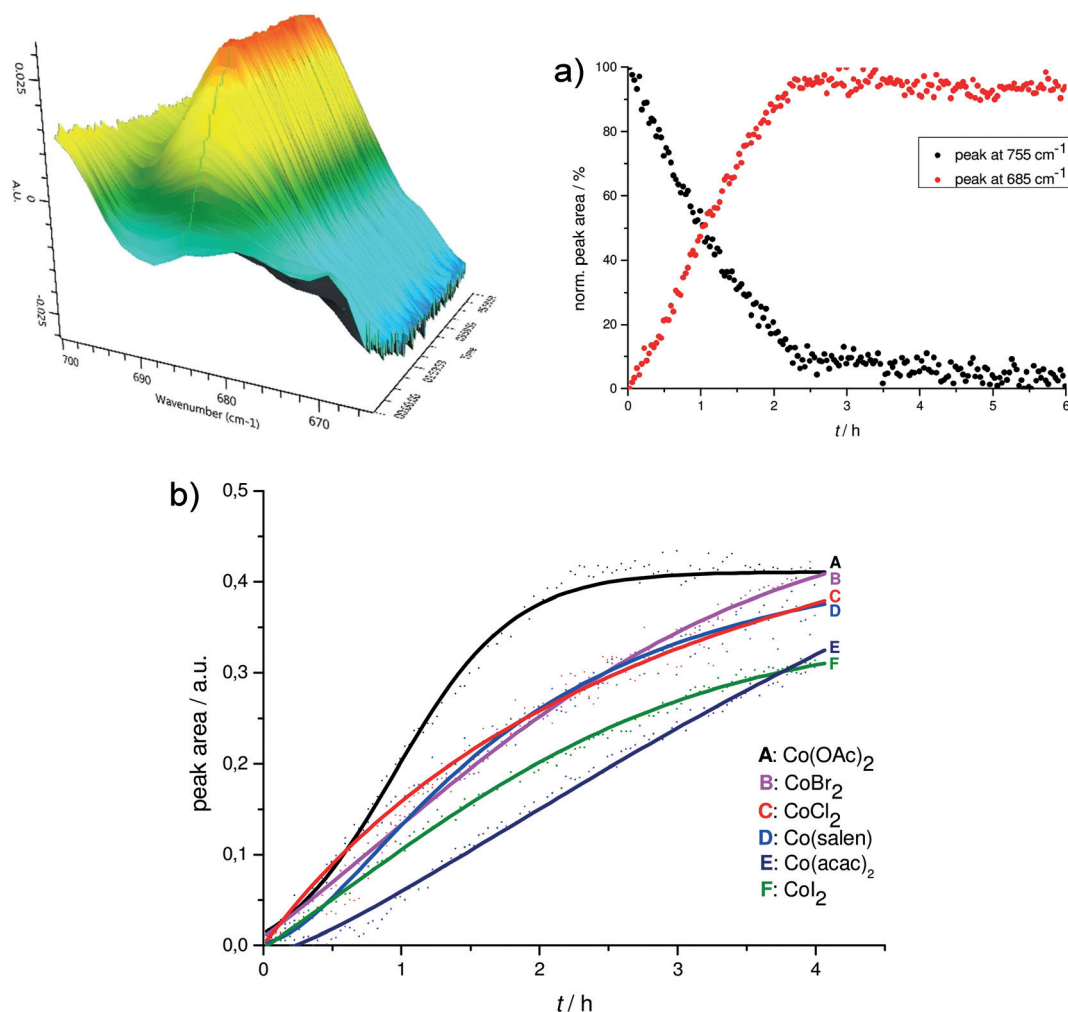

Figure 2. a) Kinetic profile with 3D surface plot. b) Comparison of various cobalt catalysts.

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 $E = -1.90$ V vs. SCE. Interestingly, the cobalt(I) complex **3** showed one irreversible reduction peak at $E = -1.82$ 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 $E = -1.70$ V vs. SCE for the reduction of cobalt(II) to cobalt(I) and $E = -1.95$ 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,
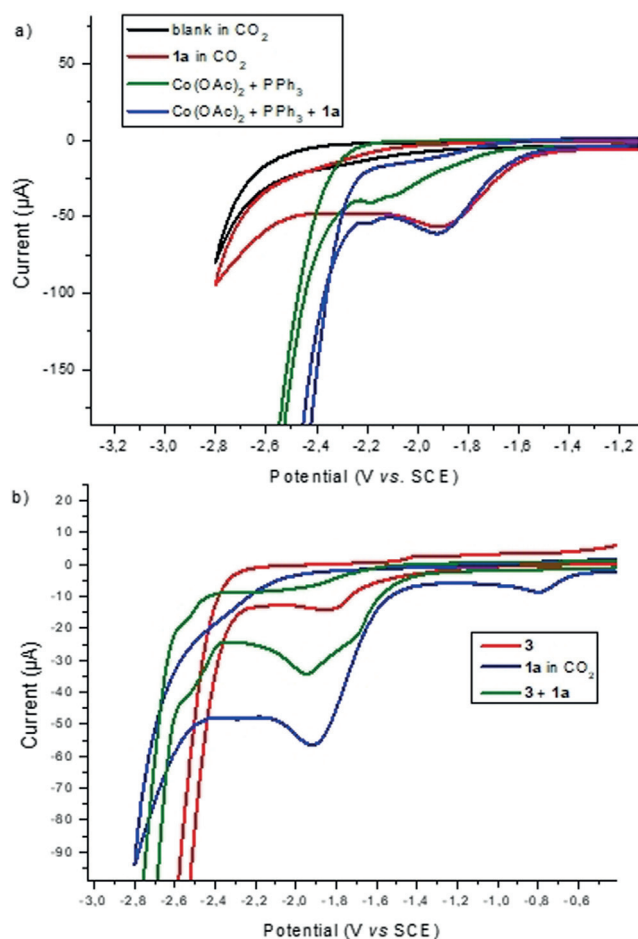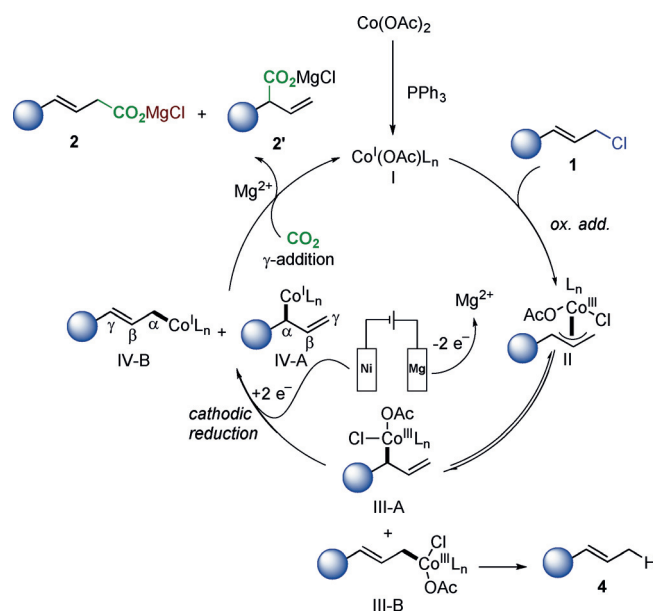
the cathodic reduction of cobalt(III) intermediate to cobalt(I) is required to facilitate the formation of the carboxylated product.

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 η^3-allyl-cobalt(III) intermediate **II**. At this stage, the intermediate **II** could undergo rearrangement to form the η^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 η^3- to η^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 η^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 γ-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.

Figure 3. Cyclic voltammetry (DMF, 0.1 M nBu$_4$NPF$_6$, 100 mVs^{-1}) with glassy carbon as the working electrode. Cyclic voltammograms of different reaction components and their mixtures. a) No interaction between simple cobalt(II) complex with **1**. b) Oxidative addition of **1** on complex **3**.

Scheme 3. Plausible catalytic cycle.

Acknowledgements

Conflict of interest

The authors declare no conflict of interest.

Keywords: carboxylation · cobalt · coupling · electrocatalysis · reduction

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