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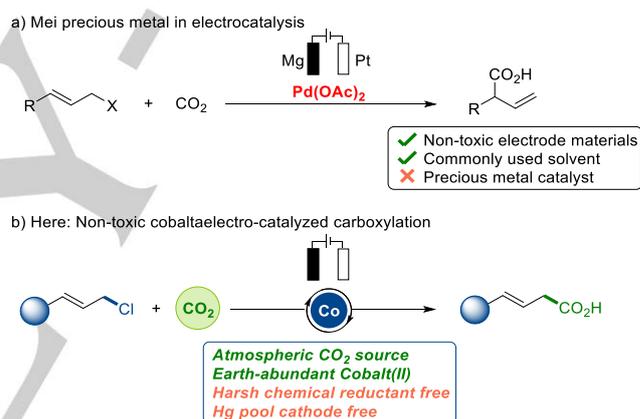
Electro-Reductive Cobalt-Catalyzed Carboxylation: Cross-Electrophile Electro-coupling with Atmospheric CO₂

Nate W. J. Ang,^[a] João C. A. Oliveira,^[a] Lutz Ackermann*^[a,b]

Abstract: The chemical use of CO₂ as inexpensive, non-toxic C1 synthon is of utmost topical interest towards a carbon capture and utilization (CCU) strategy. 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 to 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 are caused mainly by the industrialisation of raw material productions. A major component of greenhouse gases CO₂ attributes to the 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 utilisation 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 have favoured such transformations by lowering the activation energy needed.^[7] In the past, precious metals, such as palladium and rhodium, 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 toxicities.^[8b, 9] Notable examples of both precious and 3d-transition metal include Satos' studies on palladium-catalyzed carboxylations of allylic alcohols, 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 superstoichiometric amounts of manganese or zinc powder as the reducing agent.^[11] Electrocatalysis with 3d-metal catalysts^[12] has emerged as powerful tool for sustainable molecular syntheses.^[13]

Recent advances for electro-carboxylation^[14] include elegant palladium-catalyzed reductive transformations of allyl esters to useful carboxylic acids as reported by Mei (Scheme 1a).^[15] Based on precedence (Scheme 1)^[16] including the work of Perichon, where they reported an electrocarboxylation of cinnamyl chloride with the use of Hg pool cathode and Co(salen) complex.^[16e] Moreover, 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 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]



Scheme 1. Cobalt-catalysed electro-assisted carboxylation.

We initiated our studies by optimizing the reaction conditions (Table 1) on the envisioned electro-carboxylation. Different cobalt salts were used as pre-catalysts 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). A simple Co(OAc)₂ gave the best result, alongside CoCl₂ with a slight decrease in yield (see Supporting Information). Control experiments verified the important role of the electricity and cobalt pre-catalyst (entries 3–4). 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-phenantroline, performed poorly (entries 6–7).^[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 as compared with nickel foam as the cathode choice. Even though a few different anodes were tried, magnesium proved to be useful

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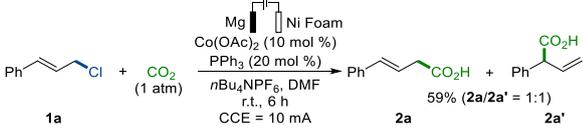
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in decreasing the high overpotential for the carboxylation to occur. Moreover, the reaction was also performed with chemical reductants, such as manganese and zinc, but to no avail even at elevated temperature (entries 13-14).^[19]

Table 1. Optimization of cobalt-catalyzed electro-reductive carboxylation^[a]

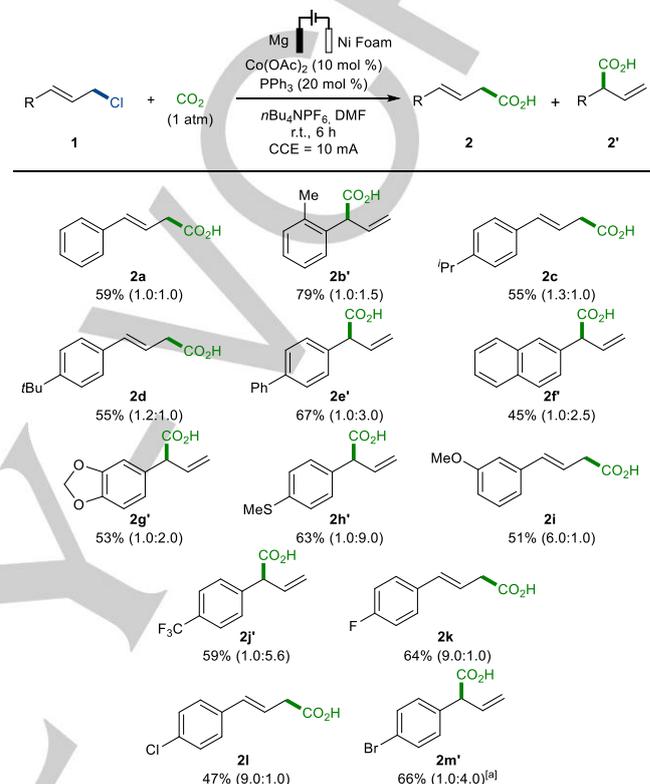


Entry	Deviation from standard conditions	Yield ^[b]
1	---	59% (1:1)
2	CCE = 5 mA	42% (1:1)
3	no current	---
4	without catalyst for 16 h	13% (1:1)
5	Co(salen) (5 mol %)	27% (1:1)
6	dppe instead of PPh ₃	27% (1:1)
7	bipyridine instead of PPh ₃	8% (1:2)
8	0.1 mol/L of 1a	44% (1:1)
9	Pt cathode	35% (1:1)
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 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 x 15 mm x 0.2 mm), Ni foam electrode (10 mm x 15 mm x 1.0 mm), constant current electrolysis (CCE) at 10 mA. [b] Isolated yield. Regioselectivity **2a/2a'** given in parentheses. [c] 2 h reaction time.

With the optimised reaction conditions in hand, we explored the substrate scope of the cobalt electro-carboxylation 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, *para*-substituted phenyl containing **2e'** and 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 for this reaction. The regioselectivity however differed as **2h'** favoured more towards the branched product, while substrate **2i** gave higher preference for the linear product. Electron-withdrawing substituents, such as trifluoromethyl **2j'**, resulted in good yield, with an 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** resulting in a higher selectivity for the linear product. The product **2m'** gave an indication that the condition was tolerated

only to a certain extent as 5-10% of the product were dehalogenated giving rise to a small mixture of **2a** in the product. This was explicitly shown when *para*-iodo containing substrate was tested and 40% of the dehalogenated product was isolated. Under otherwise identical reaction conditions, the use of alkyl-substituted and heterocyclic-substituted substrates provided as of yet unsatisfactory results.^[19]



Scheme 2. Cobalt-catalyzed electro-reductive 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**.

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 isomerisation step of η^3 -allyl complex to η^1 -allyl complex revealed to be not rate determining due to the low energy barrier of 16.1 kcal mol⁻¹ for product **2i**. Given that the electrocatalysis of the cross-electrophiles was performed at relatively high current and high CO₂ partial pressure, we direct our focus to the allylic C–C bond formation. The latter is preferred for the chlorinated substrate over the brominated substrate by 1.5 kcal mol⁻¹. Therefore, the DFT studies have shown to be in agreement with the experimentally observed regioselectivity of the product **2i**.

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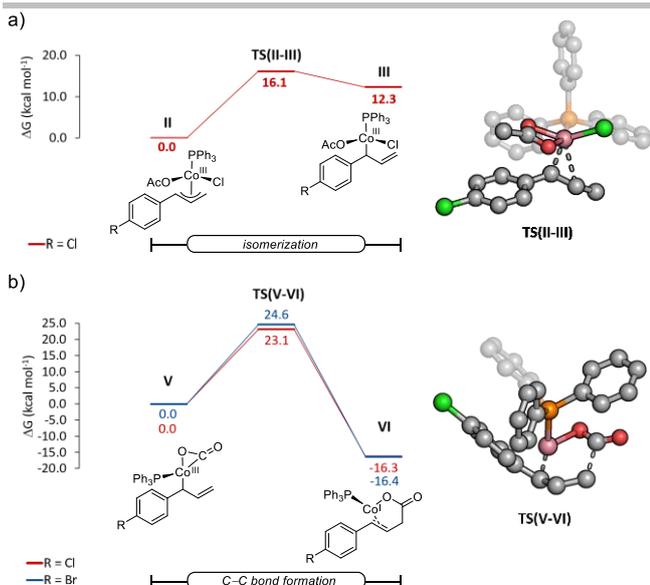


Figure 1. Computed relative Gibbs free energies in kcal mol⁻¹ for the a) isomerisation of η^3 -allyl complex to η^1 -allyl, and b) allylic C–C bond formation at the PW6B95-D4/def2-TZVPP+SMD(DMF)//TPSS-D3(BJ)/def2-SVP level of theory. Hydrogen in the computed transition state structures were omitted for clarity.

In order to understand the mechanism of this cobalt-electrocatalyzed carboxylation reaction with CO₂, we sought to investigate the mode of action. First, we elucidated the kinetic profile (Figure 2a) of the standard reaction condition together with the different simple cobalt salts as pre-catalyst for comparison in terms of the rate of reaction. An *in-operando* infra-red 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) since higher catalytic loading of Co(salen) was tried, but did not improve the yield.^[20] Second, the pre-formed 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 in the past for its use on amination reaction of unactivated aryl iodides^[21] and among others for C–H activation reactions.^[22]

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 they have a much higher potential, usually

in the positive range.^[25] These results postulated 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 CO₂ activation step. Thus, cathodic reduction of cobalt(III) intermediate to cobalt(I) is required to facilitate 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 η^1 -allyl-cobalt(III) intermediate **III-A** and **III-B** depending on different ligand effects. For instance, heteroatom such as O-atom containing ligands are known to promote 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 being employed. Here, the linear product is formed through C–C bond formation with CO₂ at the γ -position^[28] to form the carboxylated product **2** and **2'**.

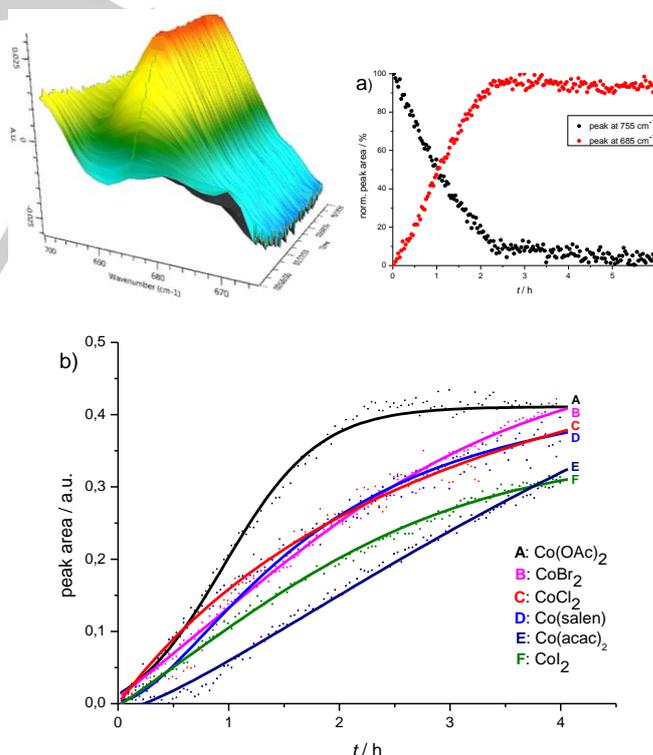


Figure 2. a) Kinetic profile with 3D surface plot. b) Comparison of various cobalt catalysts.

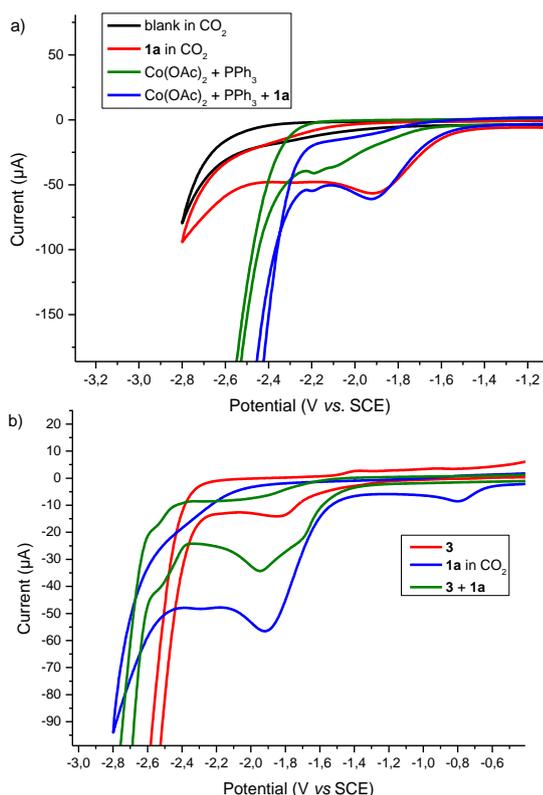
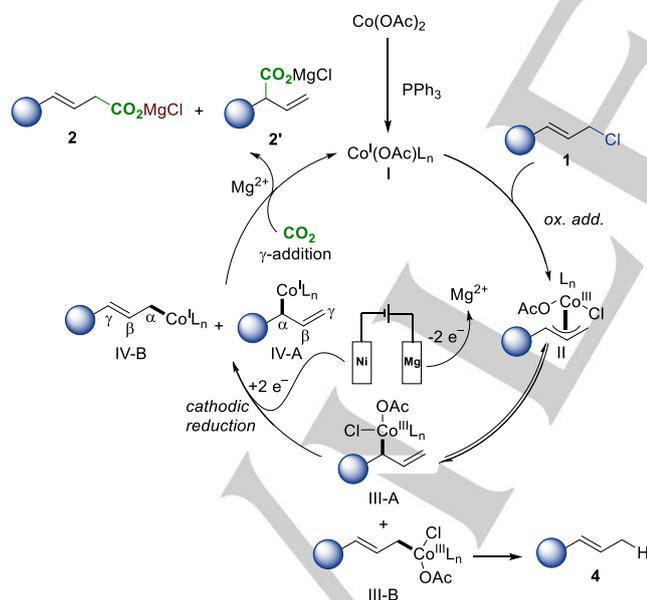


Figure 3. Cyclic voltammetry (DMF, 0.1 M $n\text{Bu}_4\text{NPF}_6$, 100 mVs^{-1}) with glassy carbon as the working electrode. Cyclic voltammograms of different reaction components and their mixtures.



Scheme 3. Plausible catalytic cycle.

In summary, we have developed an effective cobalt phosphine catalyst for the cross-electrophile electro-coupling of allylic chlorides with ambient, being devoid of harsh chemical reductants. *In-operando* IR spectroscopy and cyclic voltammetry provided detailed insights into the reaction mechanism.

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Conflict of interest

The authors declare no conflict of interest.

Keywords: cobalt • carboxylation • reductive • coupling • electrocatalysis

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Electro-Reductive Cobalt-Catalyzed
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Cobalta-electrocarboxylation: An allied co-operation between cobalt catalysis and electrochemical synthesis enabled the mild catalytic carboxylation of allylic chlorides with atmospheric CO₂.