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Advances in the Transition Metal Catalyzed Carboxylation of Aryl Electrophiles: a Field Full of Opportunities for the Brazilian Chemical Society

Avanços Envolvendo a Carboxilação de Eletrófilos de Arila Catalisada por Metais de Transição: uma Área Repleta de Oportunidades para a Sociedade Brasileira de Química

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Currently, the world faces a climate change that is correlated with CO_2 emissions by humankind, thus scientists from different fields are constantly working on methods to use or capture this released CO_2. Carbon dioxide is the holy grail for a C1 building block due to its high abundance, low cost and reduced toxicity. Enlighted by this, several groups have reported catalytic procedures to convert aryl electrophiles into the corresponding carboxylic acids. A general overview of these procedures will be covered, detailing each methodology's main advantages and limitations. Finally, the main opportunities for further innovation in this field will be listed and discussed.

Keywords: Carboxylation; palladium; nickel; copper; catalysis; cobalt.

1. Introduction

Since the first industrial revolution, the concentration of CO_2 in the atmosphere has been dramatically increasing, and this can be one of the major drivers of the current climate change we are facing.[1,2] Carbon dioxide is a greenhouse gas and given the climatic catastrophe we face, scientists are looking for alternative ways to use and capture/store CO_2.[3–8] The use of CO_2 in chemical reactions is highly desirable due to its low cost, high availability, and low toxicity which could make it an ideal C1 source.[9,10] Alas, its use also present drawbacks, which are mainly related to CO_2 being thermodynamic stable and/or kinetically inert, thus requiring either its activation or the use of very reactive species for it to participate in chemical reactions.[11,12] The reaction of strong carbon nucleophiles (such as Grignard reagents or organolithium compounds) with CO_2 has been previously described in depth, but the reaction suffers from poor functional group tolerance and uses of stoichiometric amounts of transition metals.[13,14] Thus, scientists discovered that transition metals can facilitate CO_2 insertion which has lead to a promising area in catalysis and organic synthesis. Although the field of reductive catalytic carboxylation reactions has been thriving in academic settings, its transposition to the chemical industry is still sparse. This highlights that further development of the reaction conditions to obtain a simpler and more robust catalytic system is necessary to bridge academic research and industrial applicability.[15]

Figure 1 highlights the timeline concerning publications on carboxylation reactions of aryl electrophiles. As shown, a growing development in this field has emerged, especially since the beginning of the 21st century.

This current review aims to shed light on the current and past developments of reductive catalytic carboxylation reactions of aryl electrophiles. Thus, this review is divided in two sections, the first involving the development of transition metal-catalyzed carboxylation of aryl electrophiles, and the second presenting an overall perspective on how the Brazilian chemical society can help further develop this area.

2. Reductive Carboxylation of Aryl Electrophiles

The synthesis of carboxylic acids has been a search for organic chemists due to their widespread distribution in materials and pharmaceuticals. Those can be obtained, for example,

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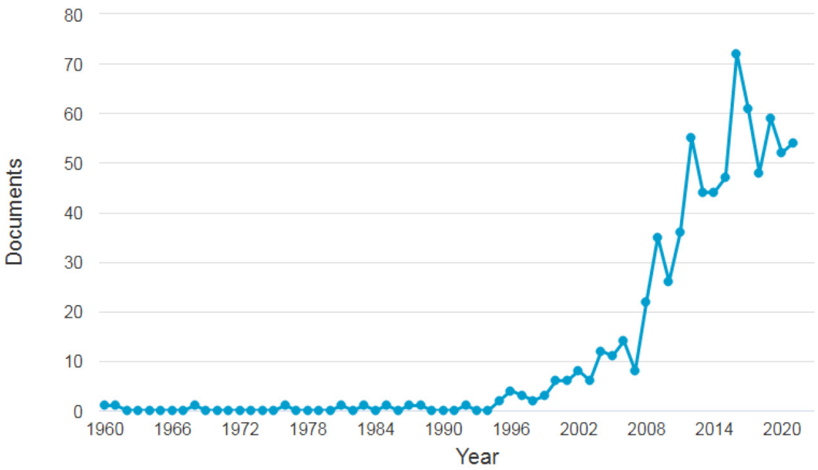
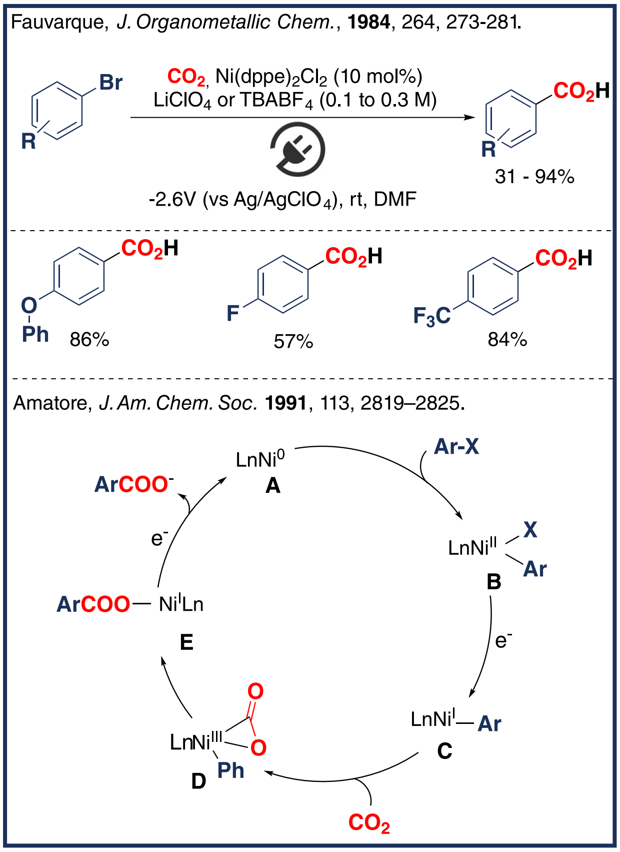


Figure 1. Published articles between 1960-2021 involving the terms "carboxylation" and "aryl" (Scopus, July 19, 2022)

from the hydrolysis of cyanides or oxidation of alcohols or aldehydes, however a direct conversion of carbon electrophiles to the carboxylic acid with the use of CO_2 is of great interest, even more, when taking into consideration the current climate goals.

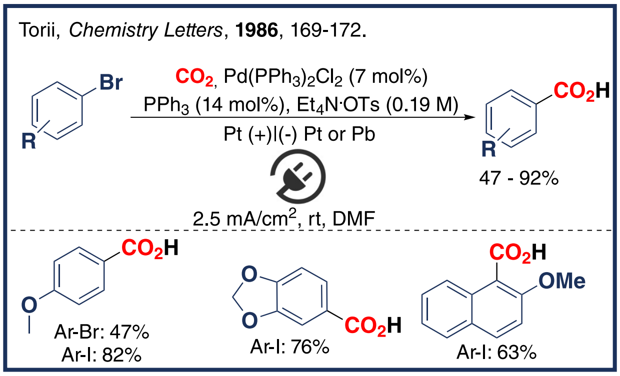
The reaction of highly reactive organolithium and Grignard reagents with CO_2 has been widely reported and although they can circumvent the kinetic stability of CO_2 due to their high reactivity, this also means limited functional group compatibility.[16] Moreover, despite that the carboxylation of aryl boronic acids and aryl zinc reagents has been extensively studied, these reagents are generally prepared by using aryl halides as starting materials. Thus, the development of straightforward catalytic methods for the direct reductive carboxylation of aryl halides was extensively pursued.

The first catalytic reductive carboxylation of aryl electrophiles was published by Fauvarque and Perichon, and it was published within the timeframe of other extensive studies on stoichiometric carboxylation reactions with Ni-Aryl complexes.[17–19] The method by Fauvarque and Perichon was an electrochemical mediated nickel catalyzed carboxylation procedure, that uses 10 mol% of $[NiCl_2(dppe)]$ as the catalyst with 0.3M $LiClO_4$ or Et_4NOTs in THF/HMPT solvent mixture (Scheme 1).[20] By using the optimized reaction conditions, although important limitations concerning the substrate scope were still observed (e.g. only *para*-substituted aryl bromides were tolerated), the desired carboxylic acids were obtained in up to 86% yield. Amatore and Jutand, that were also part of the previous report, did an in-depth study on the reaction mechanism and proposed it occurs through oxidative addition of the nickel species **A** leading to **B**, which is reduced to **C**.[21] In their studies, they also demonstrate that **C** is a key intermediate in which both the carboxylic acid or homocoupling products can be obtained.[22] If an inert atmosphere is present **C** reacts with another aryl electrophile and upon reductive elimination leads to the formation of the homocoupling product. Interestingly though if a CO_2 atmosphere is present only trace yields of the homocoupling product is observed and the carboxylic acid is obtained as the major product. Within their studies with kinetics analysis, they show that **C** reacts faster with CO_2 compared with another aryl bromide, thus leading to good yields of the desired product. For the catalytic cycle to be completed, **C** needs to undergo one more reduction, which leads to the product and recovers **A**.



Scheme 1. Nickel catalyzed electrocarboxylation of aryl bromides

This report was soon followed by the palladium-catalyzed electrocarboxylation of aryl iodides and bromides by Torri and coworkers (Scheme 2).[23] In this publication 7 mol% of $(PPh_3)_2PdCl_2$ was used, leading to the formation of the desired carboxylic acids in up to 92% yield. The high catalyst loading and the small scope presented are the main drawbacks of this protocol. Besides, a considerable decrease in yields was observed (only 47% yield) when electron-rich aryl bromides were employed. The use of substituted naphthyl iodides was also demonstrated, affording the desired carboxylic acid in 63% yield. A piperonyl-containing derivative could be synthesized from the aryl iodide starting material in 76% yield, but no other more complex molecules were presented in the scope. Other setbacks are the large excess of CO_2 which was required, the use of precious metals as cathodic material, and the use of Pb, which raises concerns related to its toxicity. A detailed mechanism with a study of which species does the CO_2 insertion was not proposed, but it was described that an oxidative addition followed by reduction of the catalyst is required.



Scheme 2. Palladium-catalyzed electrocarboxylation of aryl iodides and bromides

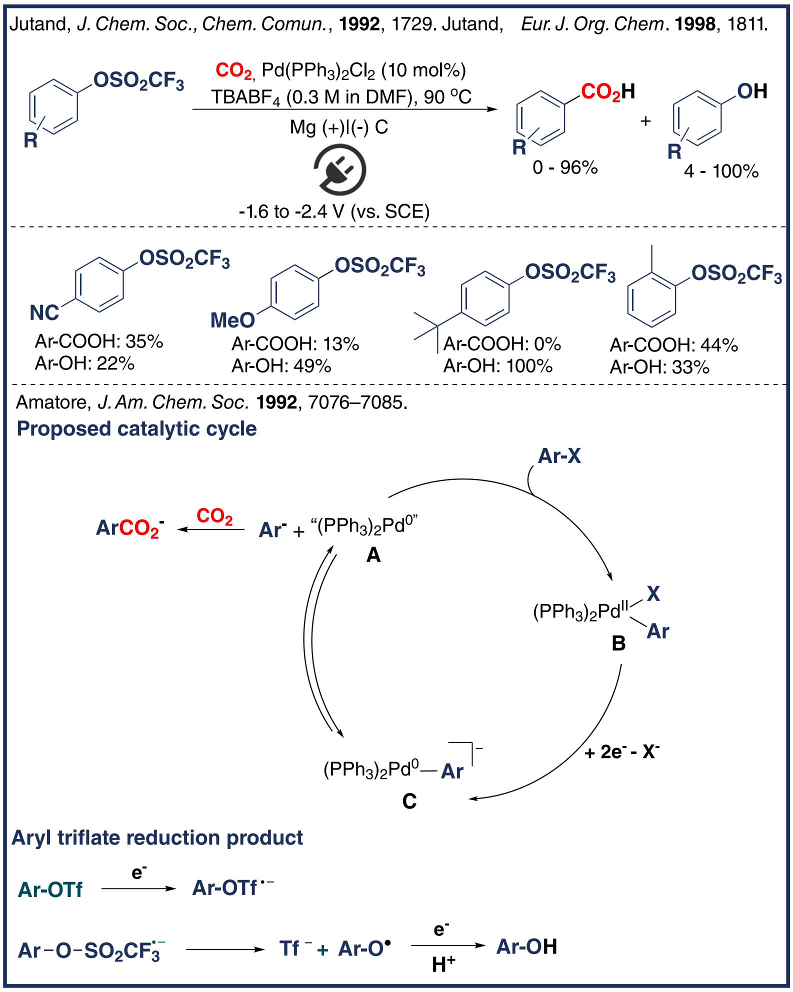
More recently, Jutand and coworkers published a set of papers in which they performed an in-depth study on the mechanism of the palladium-catalyzed electrocarboxylation reaction, which use aryl triflates as starting materials.[24–26] In general, the reported conditions were similar to the previous reports, but employed a higher catalyst loading and magnesium as a sacrificial anode. By using the optimized reaction conditions, the desired compounds were obtained in up to 96% yield (Scheme 3). It is important to point out that they observed the formation of phenols in up to quantitative yields, which are proposed to come from the direct reduction of the aryl triflates. Although a small scope was presented, allowing the use of aryl triflates bearing both electron-withdrawing or donating groups, the yields were in general only low to moderate. Selected limitations from the scope are presented (Scheme 3), and highlight that the phenol side product is the major drawback of such method.

Albeit this being the first report of catalytic carboxylation of aryl triflates, further development was still required, in particular involving the decrease in the catalyst loading and avoiding the use of magnesium as a sacrificial anode. The proposed reaction mechanism initiates with Palladium(0) performing oxidative addition into the aryl halide or pseudohalide leading to a palladium(II) complex **B** (Scheme 3). In the case of the di-triphenylphosphine ligand system, it was demonstrated by cyclic voltammetry studies that **B** undergoes a two-electron transfer leading to palladium species **C**, which is in equilibrium with free $(PPh_3)_2Pd(0)$ and aryl anion that reacts in the presence of CO_2 generating the carboxylate that upon acidic workup leads to the desired carboxylic acid.

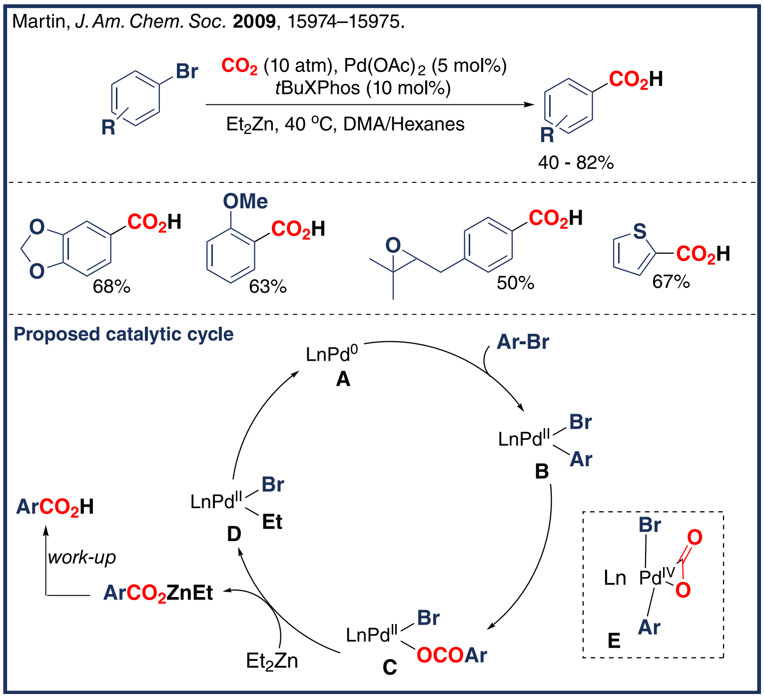
After these initial papers, studies involving aryl electrophiles catalytic carboxylations remained underdeveloped until 2009, when Martin and coworkers demonstrated the use of *t*BuXPhos as a ligand in combination with Palladium catalysis, which represented a major change from previous works (Scheme 4).[27] Additionally, instead of performing bulk electrolysis to reduce the palladium catalyst, the authors decided to use Et_2Zn as a transmetalation reagent, that enables reductive elimination, albeit leading to the Negishi coupling as a side product. Thus, aryl bromide substrates could be converted to the desired carboxylic acid in up to 82% yield. Interesting examples were prepared using this protocol; for example, Sesamol derivative was obtained in 68% yield and even sterically hindered electron-rich electrophiles such as 2-bromoanisole was well tolerated, affording the desired carboxylic acid in 63% yield. A *para*-substituted aryl group bearing an epoxide moiety was also tolerated and lead to the desired product in 50% yield. Besides, heteroaryl groups, such as thiophene could also be employed using the developed conditions, affording the carboxylic acid in 67% yield.

The proposed catalytic cycle begins with the Pd(0) oxidative addition into the aryl bromide, leading to **B** which is proposed to perform a challenging CO_2 insertion, yielding Pd^{II} complex **C.** Thereafter complex **C** undergoes a transmetalation reaction with diethyl zinc (driven by the higher electronegativity of Pd) to generate a zinc carboxylate and **D**, which ultimately recovers the catalyst and provides the desired carboxylic acid upon acidic workup. Although the proposed catalytic cycle involves Pd(0) and Pd(II) species, intermediate **E** (Pd(IV)) could not be ruled out, and it leads to **C** after reductive elimination. Additionally, **B** can also undergo transmetalation with diethyl zinc, which yields the Negishi coupling product after reductive elimination. Although better yields and a broader substrate scope was presented when compared with previous reports, this study still required the use of high catalyst loadings (5 mol%), high CO_2 pressure, amide solvents, and the use of stoichiometric metals.

A few years later, Tsuji and coworkers described a nickel-catalyzed process that uses metallic manganese as the sacrificial reducing agent (Scheme 5).[28] The catalytic system consists of $[NiCl_2(PPh_3)_2]$ with additional



Scheme 3. Palladium-catalyzed carboxylation reactions presented by Jutand and coworkers and mechanistic proposal



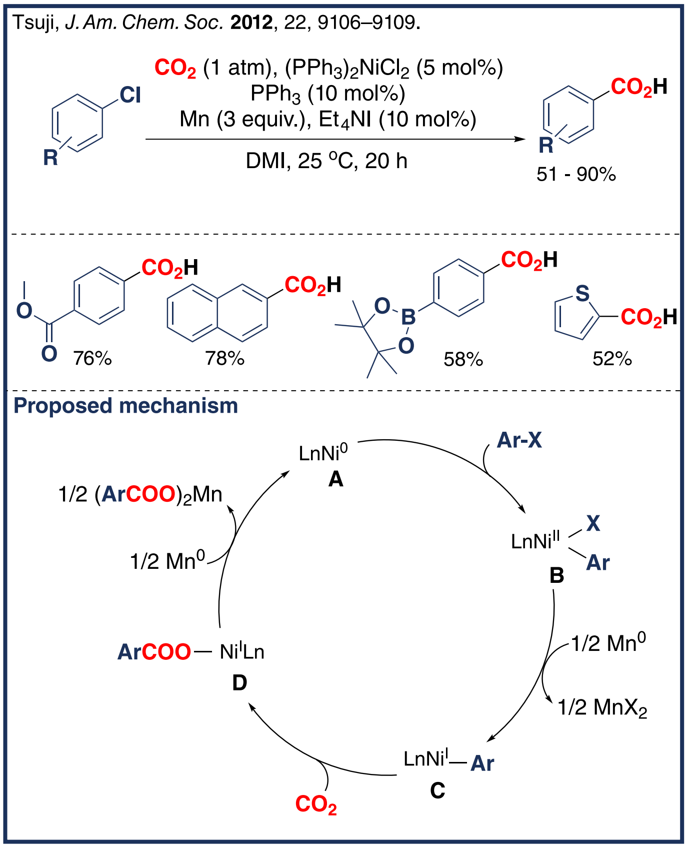
Scheme 4. Palladium-catalyzed carboxylation reaction using Et_2Zn

triphenylphosphine and tetraethylammonium iodide as additives, the desired carboxylic acids could be obtained in up to 90% yield. Although the same catalyst loading as the previous report by Martin was employed, the use of nickel (which is considerably cheaper) instead of palladium presented an important advance. Albeit the improvement in the catalytic conditions, it still required additional phosphine ligands, a high catalyst loading, the use of additives, and an amide solvent. A scope of 14 molecules was presented in which esters and boronates could be tolerated in 76% and 58% yield, respectively. Besides, a thiophene carboxylic acid could also be obtained in a 52% yield, and 2-naphthoic acid was synthesized in 78% yield.

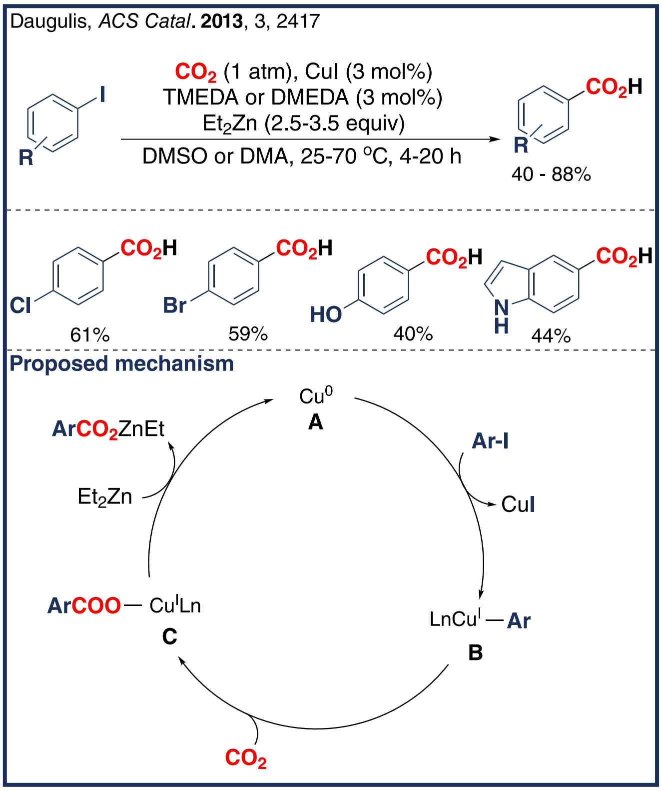
The proposed mechanism initiates with the oxidative addition into the aryl electrophile, leading to a nickel(II) species **B**. Next, **B** is reduced by single electron reduction to form the nickel^I species **C**, in which the CO_2 insertion occurs leading to **D**. Lastly, a second single electron reduction of **D** releases the product and regenerates the catalyst. Although triflates and tosylates could be applied, only three examples were demonstrated for these aryl electrophiles. Three examples involving the use of vinyl chlorides were also presented, leading to the products in up to 77% yield.

In addition to palladium and nickel, copper has also proven to be a useful catalyst for reductive carboxylation of aryl electrophiles (Scheme 6).[29] In this study the catalytic system consisted of copper iodide with amine ligands, also requiring the use of an excess of diethyl zinc, in the presence of DMSO or DMA as the solvent. As the main drawbacks, the high loading of zinc additive (2.5-3.5 equivalent), and the solvents in which the reaction was carried out presented limitations. A scope of 19 aryl iodides was presented and the products could be obtained in up to 88% yield. Both 1-bromo-4-iodobenzene and 1-chloro-4-iodobenzene could be tolerated, chemoselectively leading to the desired carboxylic acids in 61 and 59% yield, respectively. Interestingly, these motifs could be further applied in cross-coupling reactions. Additionally, 4-iodophenol could be successfully applied in the reaction conditions leading to the 4-hydroxybenzoic acid in 40% yield. Notably, unprotected indole could also be tolerated and the product was obtained in 44% yield. Although a representative scope of molecules was presented, no complex molecules were reported.

The mechanistic proposal consists of copper(0) oxidative addition into the aryl iodide, leading to the copper(I) complex **B**, in which CO_2 insertion occurs affording the copper carboxylate **C**. To further elucidate the reaction mechanism the mercury test was performed, and lower yields were obtained, an indication of an amalgam formation between copper nanoclusters and mercury, that hinders catalysis. Although this is the traditional conclusion from the mercury test, a more in-depth view on the test was done by Ananikov and coworkers, in which they show that other deactivation pathways can occur with palladium and



Scheme 5, Nickel catalyzed carboxylation of aryl electrophiles by Tsuji and coworkers



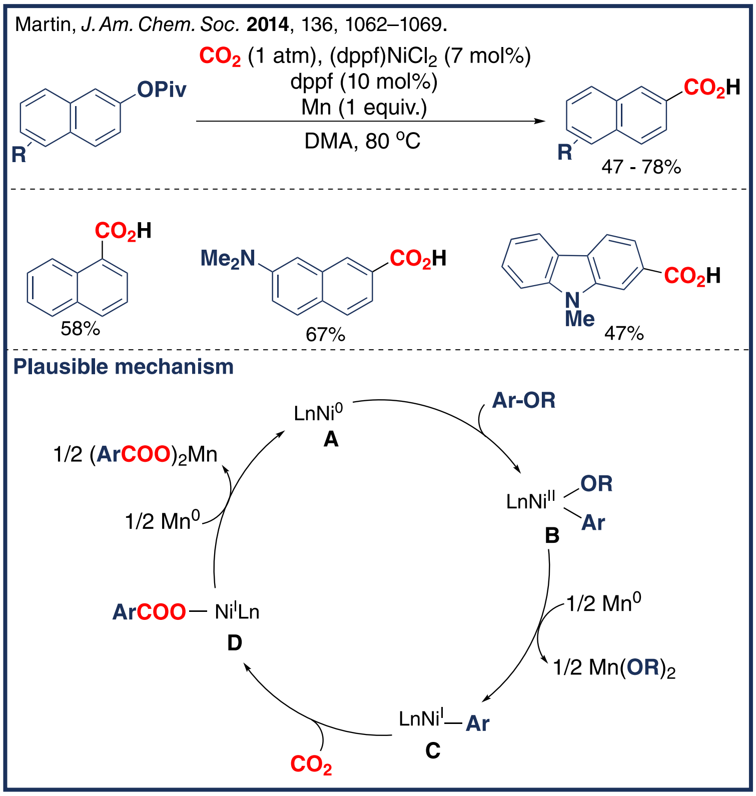
Scheme 6. Copper-catalyzed carboxylation of aryl iodides by Daugulis and coworkers

platinum homogeneous catalysis.[30] The reaction between **C** and diethylzinc leads to the zinc carboxylate that, upon acidic workup, leads to the product. The alkyl copper motif that is formed is proposed to decompose, leading to the regeneration of the copper(0) catalyst.

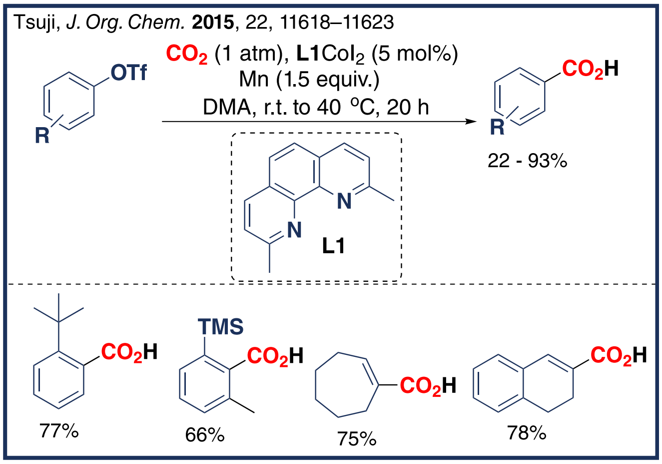
In the following year, Martin and coworkers developed a nickel-catalyzed carboxylation method for aryl pivalates with manganese as the sacrificial reducing agent (Scheme 7).[31] The reported procedure requires 7 mol% of [$NiCl_2$(dppf)] as the pre-catalyst, with an additional 10 mol% of the dppf ligand. Notably, although a high catalyst loading was required and DMA was used as solvent, it is important to point out that C (sp^2)-O bonds are quite inert and their activation is more challenging than the bonds of aryl halides. The authors observed that bulky esters are required for good yields and proposed that those might stabilize transient nickel species within the catalytic cycle. Thus, pivalates were chosen due to better atom economic and easier purification, and a variety of naphthyl pivalates and protected carbazoles were able to undergo carboxylation. As important examples, the naphthyl carboxylic acid was obtained in 58% yield and *N*,*N*-dimethyl substituted naphthyl carboxylic acid was synthesized in 67% yield. Although protected, *N*-methyl carbazole carboxylic acid could be obtained in 47% yield. The mechanistic proposal resembles the proposal by Tsuji and coworkers (Scheme 5), but instead of oxidative addition into an aryl halide or pseudo halide the oxidative addition occurs into the C (sp^2)-O bond.

The use of cobalt as catalysts for the carboxylation of aryl and vinyl triflates has also described (Scheme 8).[32] This protocols employed methyl substituted phenanthroline as the ligand and provided the products in up to 93% yield. A scope was described using 13 vinyl triflates and 7 aryl triflates as substrates. It is worth mentioning that even sterically hindered 2–(*tert*-butyl)phenyl triflate and a 2-TMS substituted phenyl triflate could be tolerated, leading to the desired carboxylic acids in 77% and 66% yield, respectively. On the contrary, the reaction failed when di-*ortho*-isopropylphenyl triflate was employed as the substrate. The use of vinyl triflates was also described, with cyclohept-1-en-1-yl trifluoromethanesulfonate affording the desired product in 75% yield, and a conjugated vinyl triflate leading to the desired product in 78% yield. Although a different catalytic system was employed, allowing the use of both vinyl and hindered aryl electrophiles, the stoichiometric manganese reducing agent and the amide solvent were still required, furthermore a mechanistic study was not presented.

During the past decade, a resurgence of photoredox-mediated processes has occurred within organic synthesis.[33] In this context, König and coworkers reported a photoredox-mediated nickel-catalyzed carboxylation of aryl electrophiles (Scheme 9).[34] The previous limitations involving the use of metallic manganese were circumvented by the use of a photoredox catalyst, which mediated the reduction of the nickel catalyst. Thus, the reducing agent could be exchanged for a soluble electron donor Hantzsch ester (HEH). Besides,



Scheme 7. Nickel catalyzed carboxylation of aryl pivalates by Martin and coworkers

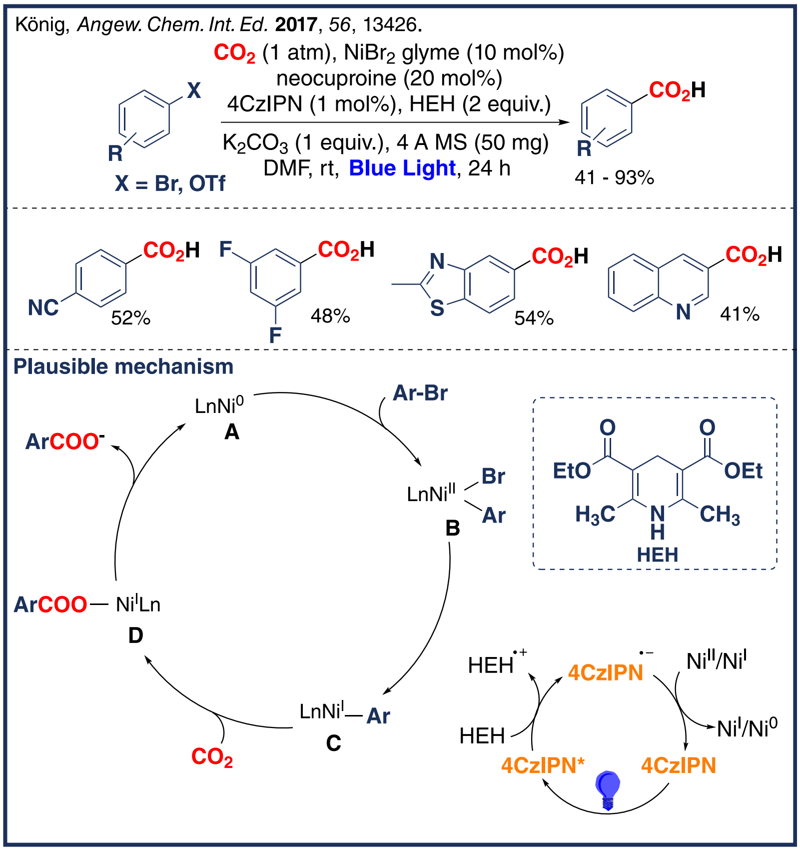


Scheme 8. Cobalt catalyzed carboxylation of aryl and vinyl triflates

in addition to the catalytic system and electron donor, the developed protocol also required the use of potassium carbonate as a base and molecular sieves. The use of stoichiometric additives, a high catalyst loading and the use of an amide solvent appeared as the main drawbacks of this methodology. On the other hand, the use of aryl and heteroaryl derivatives was well tolerated, affording the carboxylic acids in up to 93%. For example, aryl groups bearing strong electron-withdrawing groups, such as *para*-cyano and 3,5-difluoro were obtained in a 52% and 48% yield, respectively. Morevoer, quinoline and benzothiazole carboxylic acids could be obtained in 41% and 54% yields.

The mechanistic proposal is similar to previous proposals, but in this case, the reduction (from **B** to **C**) occurs through the organic dye instead of metallic manganese; CO_2 insertion is proposed to occur in the nickel(I) complex **C**. The photoredox cycle also involves a single-electron transfer from the Hantzsch ester to the organic dye.

The same year, Iwasawa and Martin reported another photoredox-mediated carboxylation, with the use of a palladium catalyst (Scheme 10).[35] The catalytic system consisted of palladium acetate and Buchwald ligands, either *t*BuXphos or PhXPhos depending on the substrate and an iridium-based photocatalyst. The protocol also required

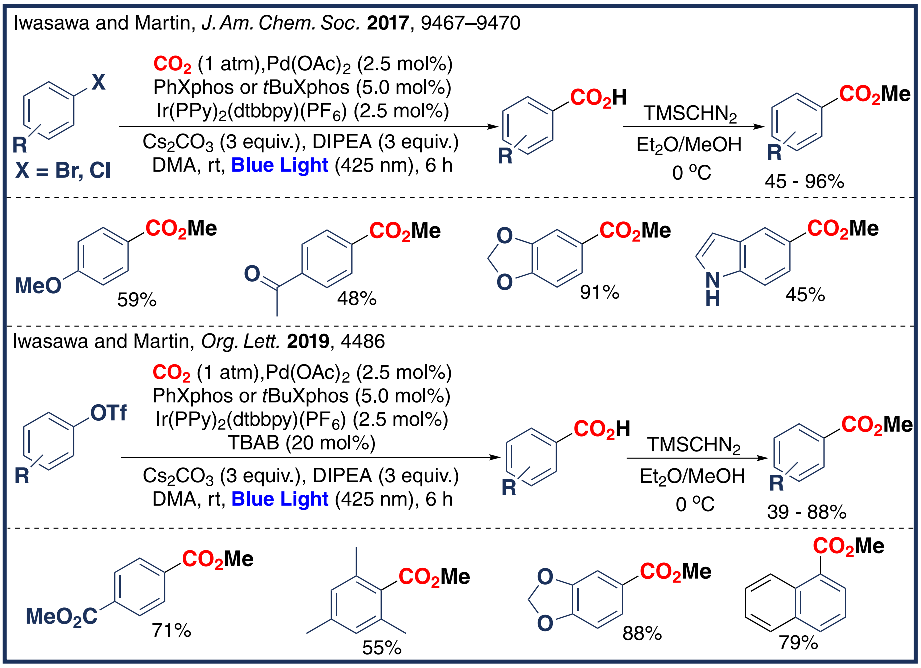


Scheme 9. Photoredox-mediated nickel catalyzed carboxylation of aryl electrophiles

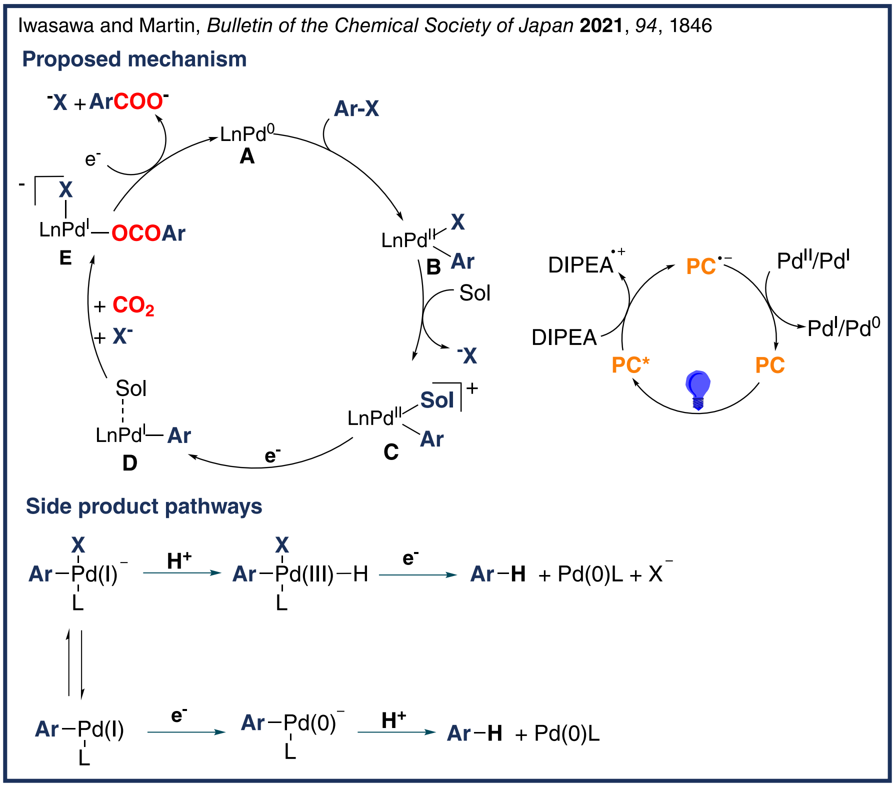
the use of cesium carbonate as a base and DIPEA as an electron donor. As the main drawbacks to this methodology, although DIPEA played the role of a homogenous electron donor it is still crude oil-based; besides, the catalyst and the iridium photocatalyst loadings are still considerably high (2.5 mol%) and amide solvents were still required. A scope of both heterocycles and substituted aromatic compounds was presented, leading to the desired methyl esters in up to 91% yield. Notably, both strong electron-donating groups, such as *para*–methoxy, and electron-withdrawing substituents, such as *para*-acetyl, were well tolerated, affording the desired products in 59% and 48% yield, respectively. Moreover, Sesamol methyl ester derivative was obtained in 91% yield and an indol-containing compound could be synthesized in 45% yield. The same authors did an in-depth mechanistic study on this photoredox-mediated methodology, and the summarized results are presented in the following Scheme 11.

The same authors, reported the carboxylation of aryl triflates using a similar catalytic system, which just required the addition of tetrabutylammonium bromide (TBAB) (Scheme 10).[36] With this set of conditions, the preparation of a representative scope of methyl esters using 9 aryl triflates and 15 vinyl triflates was reported in up to 88% yield. Notably, even the sterically hindered mesityl triflate could be converted to the methyl ester in 55% yield. As other examples, the use of a *para*-methyl ester substituted triflate and a naphthyl triflate were also tolerated, affording the products in 71% and 79% yield. Sesamol derivative was obtained in 88% yield.

In a follow-up paper, Iwasawa and Martin performed an in-depth study of the plausible catalytic cycle for the two previously described photoredox mediated processes, aiming to also answer the pathway towards the hydrodehalogenation side product (Scheme 11).[37] The mechanism begins with Pd(0) oxidative addition into the aryl electrophile, leading to palladium(II) species **B**. For aryl triflates (X = OTf), a ligand exchange of the triflate anion with the solvent is proposed, affording intermediate **C**, which undergoes single electron reduction to form the palladium(I) species **D**, that has a solvent coordinated to the complex. Then **D** undergoes CO_2 insertion, followed by another single electron reduction, that leads to the desired product and regenerates the catalyst. The authors propose that the hydrodehalogenation side product is formed due to the presence of protons in the solution, that are produced after two single electron oxidations of the amine. The cesium carbonate was employed to keep the medium basic and decrease the probability of palladium encountering a proton, especially considering that the experiments revealed that the rate of formation of the carboxylic acid and side product varies over time. Thus, it was proposed that it either occurs through the palladium(I) species interaction with a proton, leading to palladium(III) species, which



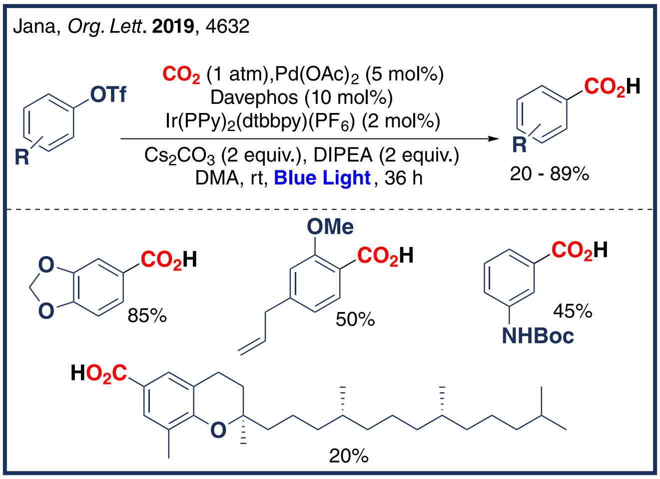
Scheme 10. Photoredox-mediated palladium-catalyzed carboxylation of aryl bromides, chlorides, and triflates



Scheme 11. Proposed catalytic cycle for the photoredox-mediated palladium-catalyzed carboxylation of aryl electrophiles by Iwasawa and Martin

can reductively eliminate the side product; or it can occur through a palladium(0) anionic species.

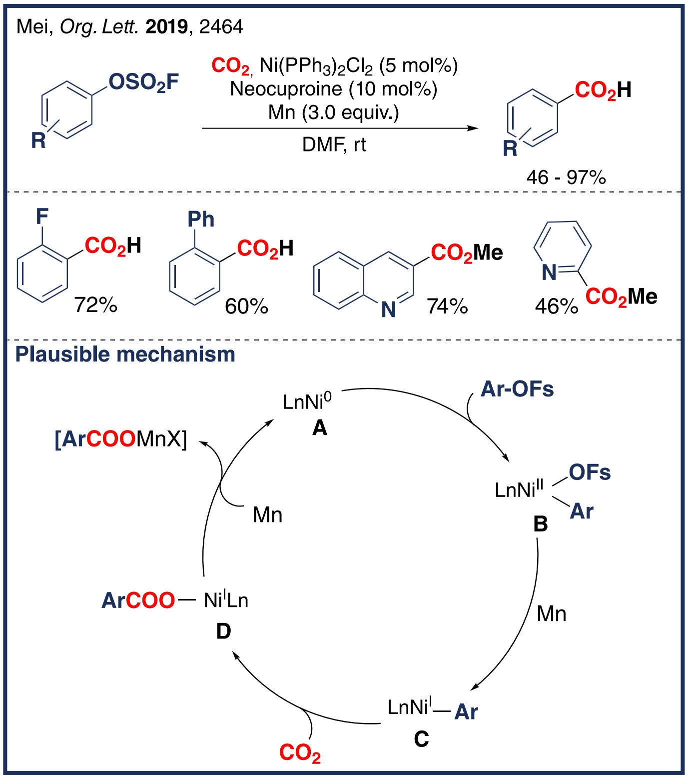
The same year, Jana and coworkers reported another method for the photoredox-mediated palladium-catalyzed carboxylation of aryl triflates (Scheme 12).[38] The catalytic system here also consisted of palladium acetate with Buchwald ligands, using Davephos as the ligand and employing a higher catalyst loading. The additives were in general similar, but employed in lower loadings, and no TBAB was required in this protocol. Sesamol and eugenol



Scheme 12. Photoredox-mediated palladium-catalyzed carboxylation of aryl triflates by Jana and coworkers

derivatives could be obtained in 85% and 50% yield, respectively. Boc-protected aniline could be converted to the carboxylic acid in 45% yield, and (+)-δ-tocopherol derivative was converted in 20% yield with 75% of starting material recovery. Albeit the moderate to good yields that could be obtained for this transformation, the high catalyst loading (5 mol%), the use of an oil-based amine as an electron donor, and the high loading of cesium carbonate appeared to be the main drawbacks of this methodology.

Recently, Mei and coworkers reported a method for the nickel-catalyzed carboxylation of aryl fluorosulfates (Scheme 13).[39] The catalytic system consists of $(PPh_3)_2NiCl_2$ and neocuproine, with metallic manganese as the reducing agent, resembling the previous catalytic system used by Tsuji and coworkers. Similarly, the same setbacks involving the amide solvent, metallic reducing agent, and high catalyst loading were also found out for this protocol. Both aromatic and heteroaromatic fluorosulfates were well tolerated and provided the desired products in up to 97% yield. Sterically hindered *ortho*-fluoro and *ortho*-phenyl benzoic acids could be obtained in 72% and 60% yield, respectively. Besides, quinoline and pyridine methyl esters could be synthesized in 74% and 46% yield. The mechanism is very similar to the proposal by Tsuji and coworkers, and the CO_2 insertion



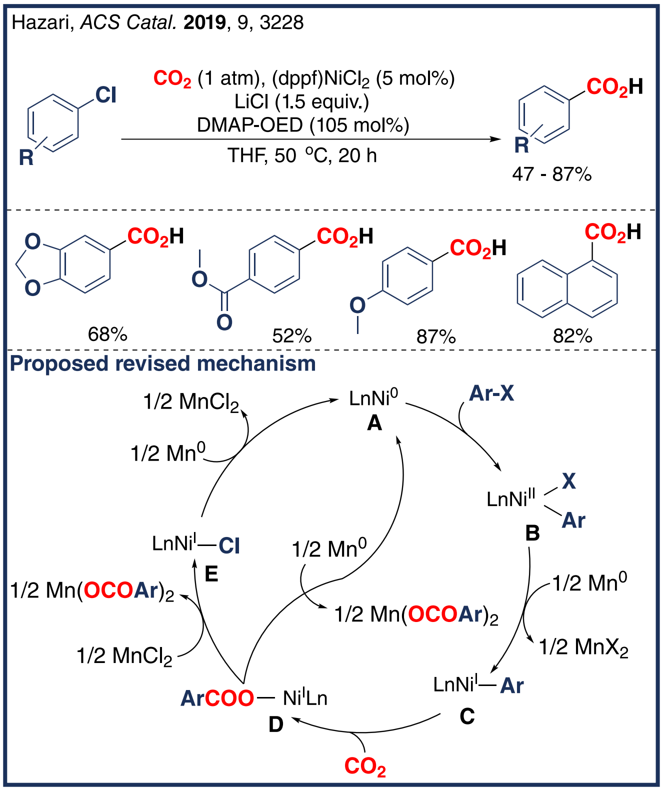
Scheme 13. Nickel catalyzed carboxylation of aryl fluorosulfates

is proposed to occur into the nickel(I) complex **C**.

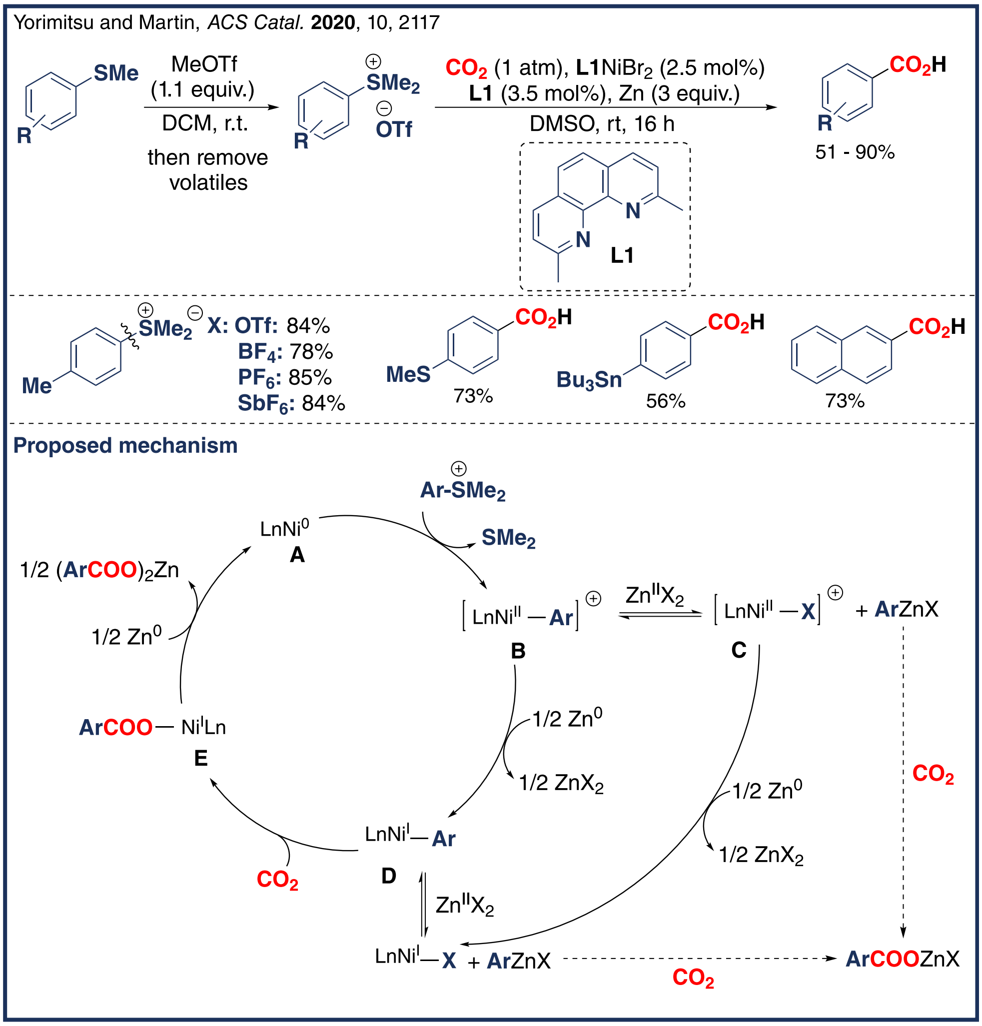
In 2019, Hazari and coworkers reported a study of the reductive carboxylation of aryl chlorides using the organic reducing agent 4,4'-bis(dimethylamino)bipyridine (DMAP-OED), which does not require the use of amide-based solvents (Scheme 14).[40] The catalytic system still required a loading of 5 mol% of [)Ni(II)Cl_2(dppf)] as the pre-catalyst and the use of LiCl, which is proposed to act as a Lewis acid and to substitute manganese chloride (normally formed *in situ* in the carboxylation reactions using metallic manganese as the reducing agent). A scope of 13 aryl chlorides was presented, including the preparation of sesamol derivative in 68% yield. Both electron-withdrawing (*para*-methyl ester) and donating (*para*-methoxy) groups could also be tolerated in 52 and 87% yield, respectively. Furthermore, the naphthyl carboxylic acid could be obtained in 82% yield. This report points out that a better mechanistic understanding of the reaction mechanism (including the catalytic cycle) can lead to further improvement of the reaction conditions. Although this is not yet a conclusive solution due to the high catalyst loading and cost of the sacrificial reducing agent, it is a great step towards the understanding of such reactions.

Within their in-depth mechanistic studies they proposed a revised catalytic cycle of the traditional nickel catalyzed carboxylation in which a ligand metathesis step from **D** with manganese chloride leads to **E**, which is reduced by manganese to recover the catalyst (Scheme 14). Additionally, **D** can also go through direct reduction, leading to carboxylate coordinated to manganese(II) and regenerating the catalyst. With the studies a participation of manganese in the catalytic cycle, besides that of a reductant was observed, thus, Hazari and coworkers demonstrated that lithium chloride is a cheap alternative, but requires the use of DMAP-OED as a reducing agent.

Recently, Martin and Yorimitsu developed a reductive carboxylation method for aryl sulfonium salts which are generated from the reaction between aryl sulfides and methyl triflates (Scheme 15).[41] After the formation of the aryl sulfonium salt, the catalytic carboxylation requires 2.5 mol% of nickel precursor, 3.5 mol% of ligand and 3.0 equivalents of zinc. Although the procedure does not require amide-based solvents, the use of over-stoichiometric loadings (3.0 equivalents) of metallic zinc is still mandatory. In the mechanistic proposal, zinc plays a dual role, acting both in the reduction of nickel and acting as a reservoir of the aryl group (forming arylzinc species that are prone to transmetalation to Ni(I) and then undergo carboxylation). The authors propose that although these arylzinc species can be formed as intermediates, zinc probably do not play a crucial role during the carboxylation step (stoichiometric studies with well-defined arylzinc triflates gave poor yield unless in presence of nickel catalyst and metallic zinc – doted lines at Scheme 15). A scope of aryl derivatives and salts with different cations was also presented to demonstrate the reaction generality. Triflate, tetrafluoroborate, hexafluorophosphate, and hexafluoro antimonate salts provided similar yields (78-85% yield) for



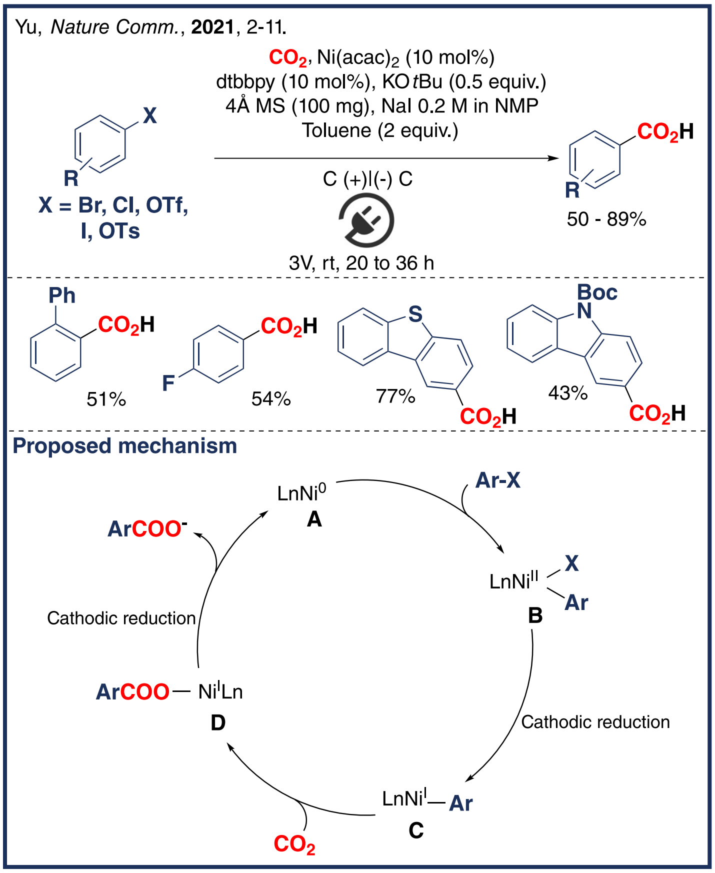
Scheme 14. Nickel catalyzed carboxylation of aryl chlorides with organic reducing agent and no amide solvent



Scheme 15. Nickel catalyzed carboxylation of aryl sulfonium salts

the *para*-methyl substituted aryl sulfonium salt. Furthermore, both electron-withdrawing (*meta*-trifluoromethyl) and donating (*para*-thiomethyl) groups were well tolerated, affording the desired compounds in 54% and 73% yield, respectively. 4-(tributylstannyl)benzoic acid could also be obtained in 56% yield, and a naphthyl benzoic acid could be synthesized in 73% yield. Although the current report did not solve the use of metallic reducing agents, it is still an important demonstration of the use of aryl sulfonium salts as cross-coupling reagents, instead of the more generally applied aryl halogens. On the other hand, the need for the previous formation of the aryl sulfonium salt from the aryl thioether represented a drawback of this methodology.

More recently, the development of novel electrochemical protocols for these transformations have also been described. For example, Yu and coworkers developed an electrochemical mediated nickel catalyzed carboxylation of aryl electrophiles (Scheme 16).[42] The catalytic system consists of [Ni(acac)$_2$] and 4,4'-di-*tert*-butyl-2,2'-bipyridine as the ligand. Besides, potassium *tert*-butoxide was required as a base, sodium iodide in NMP was used as electrolyte and solvent, and additives, such as MgBr$_2$, were also required for some substrates. In this report, the authors presented the possibility of using both a divided cell or an undivided cell setup. The undivided cell procedure, a zinc plate was used as a sacrificial anode, which did not improve the use of stoichiometric metals for the reduction of the catalyst. For the divided cell setup, the use of carbon felt electrodes on both sides was described and toluene or Et$_3$N were employed as sacrificial electron donors in the anodic cell. Although these compounds are not sacrificial metallic compounds, they are still oil-based and also the reaction was performed in an amide solvent, furthermore, in some cases the obtained faradic yields can go as low as 16%. A general scope of aryl bromides and chlorides was presented along with a few entries concerning the use of aryl triflates, tosylates, and iodides, providing the desired carboxylic acid products in up to 89% yield. The method tolerated the use of sterically hindered substrates, allowing the synthesis of *ortho*-phenyl benzoic acid in 51% yield. Fluorine-substituted carboxylic acids could also be obtained in 54% yield from the respective aryl bromide. Some heterocycles could be converted to the corresponding carboxylic acids, such as dibenzothiophene carboxylic acid and *N*-Boc carbazole carboxylic acid,



Scheme 16. Nickel catalyzed electrocarboxylation of aryl electrophiles

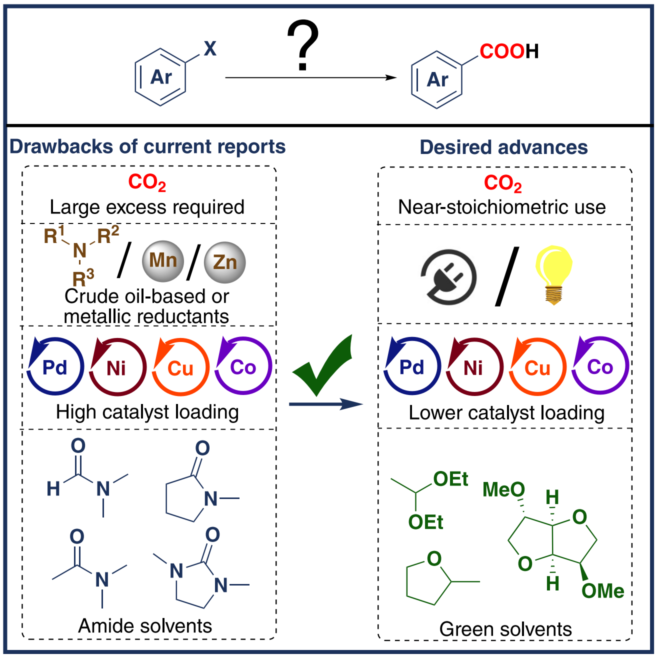
which were prepared in 77% and 43% yield, respectively. The proposed mechanism resembles the previous reports of catalytic carboxylation with nickel catalysis, in which a nickel(I) intermediate does CO_2 addition and is accessed by nickel(0) oxidative addition into an aryl electrophile followed by single electron reduction.

3. Perspectives and Opportunities for the Brazilian Chemical Society

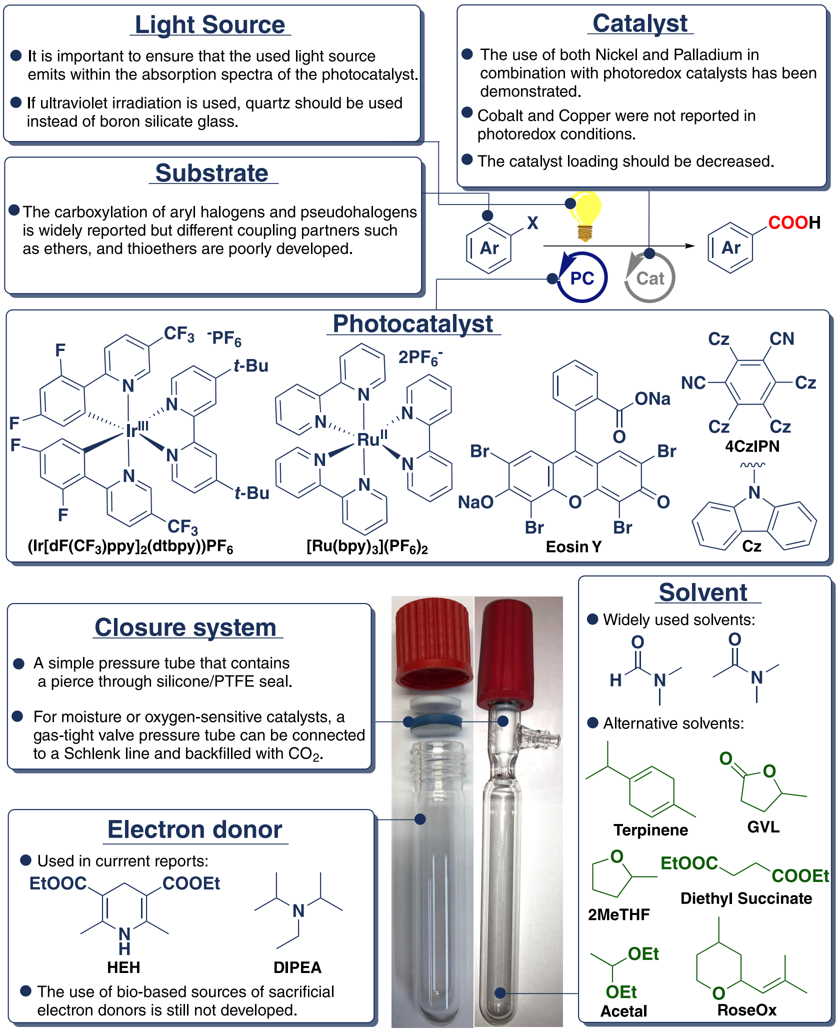
From the previously presented overview on the carboxylation of aryl electrophiles, it is important to clearly comprehend the main problems and limitations concerning this topic, aiming to search for opportunities to innovate and further develop this area (Scheme 17). This is especially true for Brazil, which still lack research groups working in this area.

The field of nickel and palladium-catalyzed CRC (catalytic reductive carboxylation) is the most studied, but also present opportunities for further advances within copper and cobalt catalysis. The use of stoichiometric amounts of metallic reducing agents should be avoided due to the related environmental and human health impacts. In this context, since a reduction of the metallic center is required to complete the catalytic cycle, two reborn approaches (photocatalysis and electrochemistry) within organic synthesis can be employed as tools for the design of novel synthetic protocols.[43–46]

The use of photoredox catalysis to mediate the organometallic catalyst reduction enabled the exchange from heterogeneous metallic reducing agents to homogeneous amines. This is feasible due to the higher oxidative and reductive potentials that can be achieved due to the excitation of the photocatalyst.[47] Although this is a major improvement, the sacrificial amines are still mainly crude oil-based, further studies could lead toward a bio-based electron donors. For scientists encouraged by such a problem and would like to further develop it, a sum of very good reviews and related publications on the topic of photoredox catalysis is selected.[48–53] For a simple reaction setup a sealed tube with a pierce-through lid can be used for this system, and the atmosphere exchange can be done with a balloon of CO_2. For more sensitive catalysts, a flask with a gas-tight valve that can be connected to a Schlenk line and backfilled with CO_2 should provide more reliable results. The choice of the light source, catalyst system, and photocatalyst (PC) must be carefully taken into account (Scheme 18). The dependence on amide-based solvent is a known problem in such reactions, but a deeper understanding of the reaction mechanism might present alternative strategies, as shown by Hazari and coworkers.[40] The use of bio-based solvents would be of great benefit as previously discussed in the literature.[54–58]



Scheme 17. Possible advances in reductive carboxylation studies and current means to achieve it



Light Source

- It is important to ensure that the used light source emits within the absorption spectra of the photocatalyst.
- If ultraviolet irradiation is used, quartz should be used instead of boron silicate glass.

Catalyst

- The use of both Nickel and Palladium in combination with photoredox catalysts has been demonstrated.
- Cobalt and Copper were not reported in photoredox conditions.
- The catalyst loading should be decreased.

Substrate

- The carboxylation of aryl halogens and pseudohalogens is widely reported but different coupling partners such as ethers, and thioethers are poorly developed.

Photocatalyst

Closure system

- A simple pressure tube that contains a pierce through silicone/PTFE seal.
- For moisture or oxygen-sensitive catalysts, a gas-tight valve pressure tube can be connected to a Schlenk line and backfilled with CO_2.

Electron donor

- Used in currrent reports:
- The use of bio-based sources of sacrificial electron donors is still not developed.

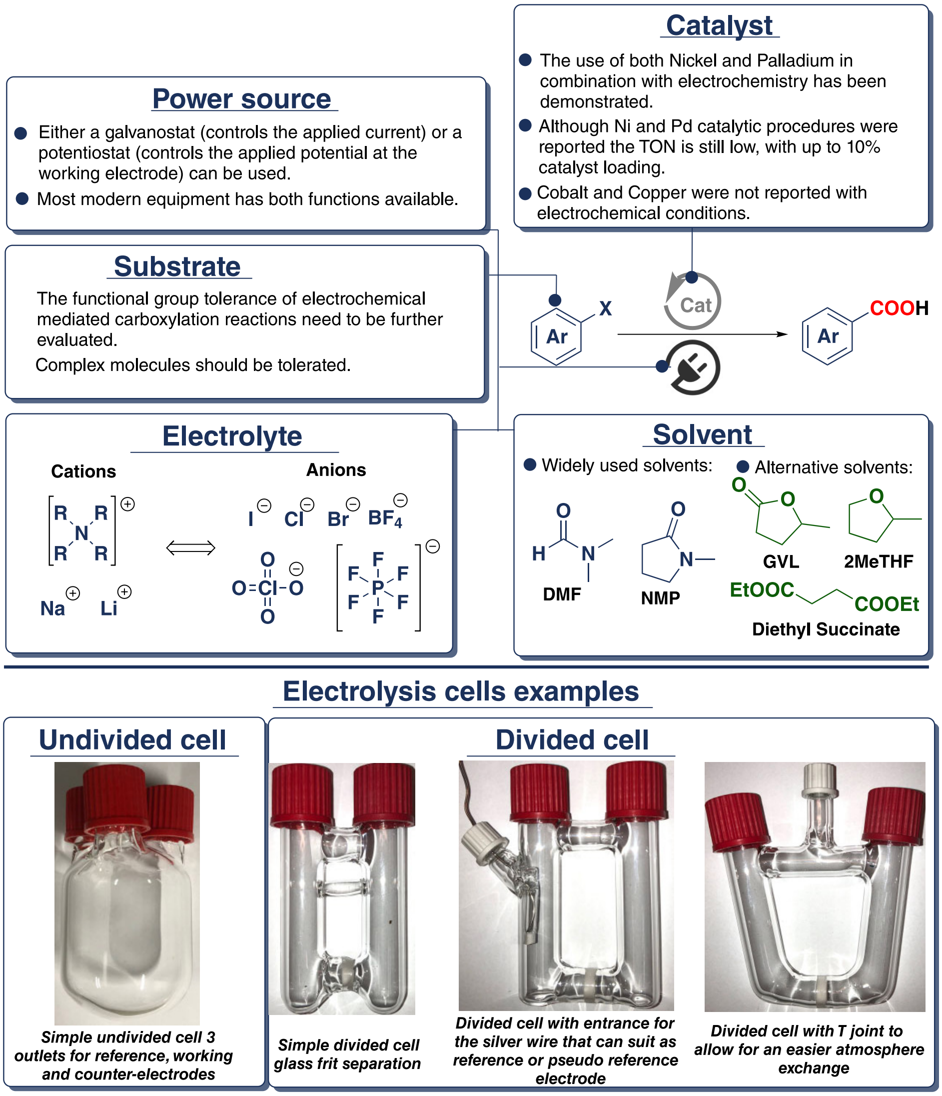
Solvent

- Widely used solvents:
- Alternative solvents:

Scheme 18. Photoredox reductive carboxylation

Besides photoredox catalysis, electrochemistry is a second tool that could assist to bridge the gap between academic research and industrial application.[59] The synthesis of value-added fine chemicals with carboxylation reactions could also aid in the green transition that the chemical industry could face in the next few years to help achieve the climate goals.[15,60] Within electrochemistry there are a few extra details one has to be aware of (Scheme 19), such as choosing the supporting electrolyte (that has to be soluble in the desired solvent), and the adequate electrode material. Although there are a lot of parameters and can be overwhelming to know where to start, the literature provides important studies which aim to introduce and guide chemists interested in performing electrosynthesis.[61,62] Additionally, it is important to know the reduction potentials of the species one is trying to reduce, cyclic voltammetry studies can be performed to obtain such values.[63] Last, within the electrolysis cell there are two options: divided or undivided cells, it is clear to observe the difference but within the divided, one can use simply a glass frit that creates a physical barrier or íon exchange membranes. These can be either cation or anion exchange membranes and are available commercially from brands such as Nafion®.[64]

Although major discoveries have been done in the field of reductive catalytic carboxylation reactions for it to become widely applied additional breakthroughs need to occur. Within the difficulties that such reactions currently face, the use of amide solvents remain as a major gap, with one outlier paper by Hazari and coworkers with the use of THF.[40] The role played by the amide solvent, besides its high CO_2 solubility is still a question that needs to be answered. Finally, further mechanistic studies of the interactions that might occur between the organometallic species and different solvents might help understand the additional roles of such solvents. Additional improvements in substrate scope, electron donor, and catalyst activity are also very relevant for further utilization of carboxylation reaction. Although reductive carboxylation reactions that don't require the use of transition metal catalysts were not covered in this review, this is still an area of great interest that could lead to important processes.[65–71]



- Either a galvanostat (controls the applied current) or a potentiostat (controls the applied potential at the working electrode) can be used.
- Most modern equipment has both functions available.

- The use of both Nickel and Palladium in combination with electrochemistry has been demonstrated.
- Although Ni and Pd catalytic procedures were reported the TON is still low, with up to 10% catalyst loading.
- Cobalt and Copper were not reported with electrochemical conditions.

The functional group tolerance of electrochemical mediated carboxylation reactions need to be further evaluated.
Complex molecules should be tolerated.

Simple undivided cell 3 outlets for reference, working and counter-electrodes

Simple divided cell glass frit separation

Divided cell with entrance for the silver wire that can suit as reference or pseudo reference electrode

Divided cell with T joint to allow for an easier atmosphere exchange

Scheme 19. Electrochemical reductive carboxylation

4. Conclusion

In chemistry, the use of low-cost and readily accessible reagents is highly desirable. In this context, the use of natural available gases, such as carbon dioxide, has attracted a growing interest in organic synthesis. Although the development of novel carboxylation protocols has increased functional group compatibility, accessing highly functionalized products is still a challenge. Furthermore, advancements in catalyst design for carbonylation reactions (and also other types of palladium-catalyzed cross-couplings) allowed the use of very low catalyst loadings with very high TON and TOF (turnover number and turnover frequency), which is normally required for bulk industrial settings and contrasts with the high catalyst loading that is still required for carboxylations.[72–76] Despite that, over the last years recent and important examples have been described, especially concerning the use of photochemistry and electrochemistry. Aryl carboxylic acids are ubiquitous motifs in pharmaceuticals, agrochemicals, and materials which highlights the importance of developing efficient methods using CO_2 for its synthesis. Unfortunately, the research on this area in Brazil is still underdeveloped, not only for concerns involving the safe handling of the gas but also for difficulties involving CO_2 activation and catalyst cost. Thus, this field presents itself as a great opportunity for researchers within transition metal-catalyzed activation of CO_2.

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