Advances in Palladium-Catalyzed Carboxylation Reactions

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Abstract: In this short review, we highlight the advancements in the field of palladium-catalyzed carbon dioxide utilization for the synthesis of high value added organic molecules. The review is structured on the basis of the kind of substrate undergoing the Pd-catalyzed carboxylation process. Accordingly, after the introductory section, the main sections of the review will illustrate Pd-catalyzed carboxylation of olefinic substrates, acetylenic substrates, and other substrates (aryl halides and triflates).

Keywords: carbon dioxide; carboxylation; catalysis; heterocycles; palladium

1. Introduction

The efficient incorporation of carbon dioxide into an organic substrate (carboxylation) under catalytic conditions to give high value added molecules is one of the most important and fascinating areas of current organic synthesis. In fact, carbon dioxide is a nonflammable, inexpensive and largely available C-1 feedstock. Moreover, the efficient conversion of CO₂ into organic compounds is a very attractive synthetic approach. In fact, it allows converting an important waste (it is well known that carbon dioxide is produced in enormous amounts from the combustion of fossil fuels for the production of energy) into a variety of useful compounds, which can find application as fuels or in the pharmaceutical or material fields. Accordingly, many efforts have been devoted by the scientific community to develop novel efficient and sustainable carboxylation methods, in particular under catalytic conditions, during the last years [1–34].

This short review is intended to present paradigmatic examples of carboxylation processes based on palladium catalysis, with particular emphasis to the more recently reported methods (coverage: from 1980ies to date). Only processes in which carbon dioxide is fully incorporated into the organic substrates will be considered, while the reactions in which CO₂ is incorporated as a carbonyl function only, resulting in indirect carbonylation rather than carboxylation, are beyond the scope of this review.

2. Palladium-Catalyzed Incorporation of Carbon Dioxide into Olefinic Substrates

Suitably functionalized olefins are excellent substrates for the Pd-catalyzed incorporation of carbon dioxide to give high value added heterocyclic compounds. For example, vinyl epoxides undergo a Pd(0)-promoted ring-opening process with formation of a π-allylpalladium alkoxide intermediate I, which can attack CO₂ to give a π-allylpalladium carbonate II that then undergoes intramolecular nucleophilic attack to give vinyl-substituted 5-membered cyclic carbonates 1, as shown in Scheme 1. This kind of process was independently disclosed by the groups of Fujinami [35] and Trost [36,37] in the 1980s; an example of synthetic application is shown in Scheme 2 (in this and in all the following schemes of the review, unreactive ligands on palladium are not shown for clarity) [38].
Scheme 1. Pd(0)-catalyzed carboxylation of 2-vinyloxirane to 4-vinyl-1,3-dioxolan-2-one 1.

In a similar manner, 5-vinyloxazolidinones 2 can be synthesized from vinylaziridines. For example, using a catalytic system consisting of Pd\(_2\)(dba)\(_3\)/PPh\(_3\)/TBAT (TBAT = tetrabutylammonium difluorotriphenylsilicate), in toluene as the solvent and under particularly mild reaction conditions (0 °C and atmospheric pressure of CO\(_2\)), a variety of 5-vinyloxazolidinones was prepared (Scheme 3). The process showed high regioselectivity and was also diastereospecific [39].

Cycloalkylidene cyclopropanes, bearing the highly reactive cyclopropane ring, have been reported to undergo ring-opening carboxylation under relatively mild conditions to yield five-membered lactones, as shown in Scheme 4 for the formation of 3 and 3' [40]. Reactions were carried out in toluene at 120 °C under 40 atm of CO\(_2\), in the presence of Pd\(_2\)(dba)\(_3\)/PCy\(_3\) as the catalytic system and dimethyl sulfoxide (DMSO) as additive. The reaction showed a certain degree of diastereoselectivity, favoring the formation of the diastereoisomer with the carbonyl group in the axial position 3 in most cases. The proposed mechanism involves the initial oxidative insertion of Pd(0) into the cyclopropane ring with formation of a four-membered Pd(II) palladacycle intermediate I, as shown in Scheme 4, which may undergo a ring opening process to give a zwitterionic π-allylpalladium complex II. The latter inserts CO\(_2\) by carbanion attack to give a carboxylate zwitterionic intermediate III (only the intermediate leading to the major diastereoisomer is shown in the scheme), from which the final product 3 is formed by intramolecular attack of the carboxylate group to the π-allyl moiety, with regeneration of the Pd(0) catalyst (Scheme 4).
Mechanistically, the reaction follows a pathway similar to that seen in Scheme 1, as the key intermediate is a zwitterionic π-allylpalladium complex I [formed by oxidative addition of the substrate to Pd(0)], which reacts with CO$_2$ to give a zwitterionic carboxylate complex II. The latter undergoes cyclization (by intramolecular nucleophilic attack of the carboxylate to the π-allylpalladium system), with regeneration of Pd(0) and formation of a 4-methylenehydrofuran-2(3H)-one intermediate III, which eventually isomerizes to the final 2(5H)-furanone product 4 (Scheme 5).

Vinyl-substituted 5-membered cyclic carbonates 5 were synthesized from allylic carbonates by a sequential CO$_2$ elimination–fixation process, as shown in Scheme 6, with formal CO$_2$ recycling, again through the formation of a zwitterionic π-allylpalladium complex I [42]. Reactions were performed in the presence of Pd$_2$(dba)$_3$ as catalyst in the presence of dpff [1,1′-bis(diphenylphosphino)ferrocene] or dppe [1,2-bis(diphenylphosphino)ethane] as ligand, in dioxane at 50 °C under inert atmosphere. The process was shown to be enantiospecific when starting from nonracemic allylic carbonates to yield nonracemic cyclic carbonates.
Scheme 6. Synthesis of 4-vinyl-1,3-dioxolan-2-ones 5 from (E)-4-hydroxybut-2-en-1-yl methyl carbonates.

In a subsequent work, the same research group reported the synthesis of dienylic 5-membered cyclic carbonates 6 from 6-methoxycarbonyloxy-2,4-hexadien-1-ols under similar conditions [Pd(dbachloror) as catalyst in the presence of dppe or dppv (1,2-bis(diphenylphosphino) ethylene) as ligand, in dioxane at 50 °C], as shown in Scheme 7 [43].

Scheme 7. Synthesis of dienylic 5-membered cyclic carbonates 6 from 6-methoxycarbonyloxy-2,4-hexadien-1-ols.

Allylamines have been reported to react with alkyl bromides and carbon dioxide (1 atm) in DMSO at room temperature, in the presence of Pd(PPh3)4 as catalyst and 1,5,7-triazabicyclo[4.4.0]dec-5-ene (TBD) as base and under visible light irradiation (10 W blue LED lamp), to give 2-oxazolidinones 7 in good yields (Scheme 8) [44]. Experimental data were in agreement with a radical mechanism, which starts with the photoexcitation of Pd(0) followed by single electron transfer (SET) with the alkyl bromide to give a Pd(I) species I and an alkyl radical II. The latter reacts with the double bond of the carbamate intermediate III formed by the attack of the amino group of the allylamine substrate to CO2 in the presence of TBD, thus leading to a radical anion species IV. This species undergoes another SET process with Pd(I) with regeneration of the Pd(0) catalyst and formation of a zwitterionic intermediate V, whose cyclization by intramolecular nucleophilic attack finally affords the oxazolidinone product 7 (Scheme 8).

Scheme 8. Synthesis of 2-oxazolidinones 7 from allylamines and alkyl bromides.
In a very similar manner, 1,4-dihydro-2\(H\)-3,1-benzoxazin-2-ones 8 were recently synthesized from 2-(1-arylvinyl)anilines, alkyl bromides, and carbon dioxide in the presence of the same catalyst [Pd(PPh\(_3\))\(_4\)] and base (TBD) and under visible light irradiation (2 × 3 W blue LED lamps), at room temperature and under atmospheric pressure of CO\(_2\) (Scheme 9) [45].

![Scheme 9. Synthesis of 1,4-dihydro-2\(H\)-3,1-benzoxazin-2-ones 8 from aryloxyallenes, aryl iodides, and amines.](image)

More recently, aryloxyallenes have been reported to undergo a multicomponent reaction with amines, carbon dioxide, and aryl iodides, catalyzed by Pd(PPh\(_3\))\(_4\) in the presence of TBD, to give 1-aryloxy-2-arylallyl carbamates 10, according to Scheme 11 [47]. From a mechanistic point of view, the process is believed to begin with the oxidative addition of TBD, to give 1-aryloxyallenes 9 from methoxylallene.

![Scheme 10. Synthesis of (E)-6-methoxy-3-(methoxymethylene)-5-methylenetetrahydro-2\(H\)-pyran-2-one 9 from methoxylallene.](image)

![Scheme 11. Synthesis of 1-aryloxy-2-arylallyl carbamates 10 from aryloxyallenes, aryl iodides, and amines.](image)
When the aryloxy and Ar–I functional groups were present in the same substrate in relative ortho positions, 3-methylene-2,3-dihydrobenzofuran-2-yl carbamates 11 were obtained by a similar sequence of mechanistic steps, the carbamate nucleophilic attack to the σ-alllyl system occurring in this case intramolecularly (Scheme 12) [48]. Interestingly, (1-tosyl-1H-indol-3-yl)methyl carbamates were selectively formed when starting from 2-iodo-N-(propa-1,2-dien-1-yl)-N-tosylanilines, by an inversion of regiochemistry in the intramolecular nucleophilic attack, probably owing to the steric hindrance exerted by the tosyl group on nitrogen.

$$\text{R}^1 = \text{H, CF}_3, \text{Cl, Br}; \text{R}^2 = \text{H, alkyl}; \text{R}^3 = \text{alkyl, aryl}$$

Scheme 12. Synthesis of 3-methylene-2,3-dihydrobenzofuran-2-yl carbamates 11 from 1-iodo-2-(propa-1,2-dien-1-yl)benzenes and amines.

In a related work, N-Boc-2-iodo-N-(propa-1,2-dien-1-yl)anilines (Boc = tert-butyloxycarbonyl) were allowed to react with ZnEt₂ and CO₂ (1 atm) and room temperature in the presence of PdCl₂ as the palladium source and P(C₆H₄-p-CF₃)₃ as ligand to give a ((1-Boc-3-methyleneindoline-2-carbonyl)oxy)(ethyl)zinc intermediate I. This was transformed into methyl 1-Boc-3-methyleneindoline-2-carboxylates 12 by acidic quenching and subsequent reaction with TMSCHN₂ (TMS = trimethylsilyl) (Scheme 13) [49].

$$\text{R} = \text{H, F, Cl, Br, CF}_3, \text{CN, Me, OMe}$$

Scheme 13. Synthesis of methyl 1-Boc-3-methyleneindoline-2-carboxylates 12 by from N-Boc-2-iodo-N-(propa-1,2-dien-1-yl)anilines.

Ikayara and coworkers reported the reaction of α-allenyl amines with dense CO₂ (11.5 MPa) to give 5-vinyl-2-oxazolidinones 13 under the catalysis of Pd(0), obtained in situ from palladium acetate, as shown in Scheme 14 [50]. The proposed mechanism starts with the formation of a carbamate intermediate I (from the reaction between the substrate and CO₂) followed by oxidative addition of the –OH group to Pd(0). Insertion of the internal allenyl double bond into the ensuing Pd–H bond then takes place, with formation of a π-allylpalladium complex II. Cyclization with reductive elimination of Pd(0) finally yields the oxazolidinone product 13 (Scheme 14).
In 1999, Inoue and coworkers reported the Pd(0)-catalyzed formation of vinyl-substituted cyclic carbonates from 2,3-dienols or 3,4-dienols, aryl or vinyl halides, and CO₂, as exemplified in Scheme 15 for the synthesis of 4-vinyl-1,3-dioxolan-2-ones 14 from 2,3-dienols and aryl halides [51]. The process, carried out in DMA (N,N-dimethylacetamide) at 50–100 °C under 40 atm of CO₂ in the presence of Pd(PPh₃)₄ as catalyst and K₂CO₃ as base, took place through oxidative addition of the halide to Pd(0), followed by insertion of the allenyl moiety of the deprotonated substrate to give a π-allylpalladium complex I. The final product 14 was then formed by attack of the anionic oxygen to CO₂ followed by intramolecular nucleophilic attack of the ensuing carbonate moiety to the π-allylpalladium system, with regeneration of Pd(0) (Scheme 15).

In a similar way, 5-vinyl-2-oxazolidinones 15 were synthesized from 2,3-allenyl amines, aryl iodides and CO₂ (1 atm) in the presence of Pd(PPh₃)₄ and K₂CO₃ as the base, in DMSO at 70 °C (Scheme 16) [52]. The reaction starts with the oxidative addition of the aryl iodide to Pd(0) to give an Ar–Pd–I complex, which inserts the allenyl moiety of the π-allylpalladium carbamate intermediate I formed by the reaction between the allenyl amine and CO₂. Intramolecular nucleophilic attack of the carbamate to the π-allylpalladium moiety eventually leads to the vinylloxazolidinone product 15 with re-
generation of Pd(0) (Scheme 16). Interestingly, the use of the ligand Gorlos-Phos[11]HBF₄ (Gorlos-Phos = dicyclohexyl(2,6-diisopropoxyphenyl)phosphane) allowed a stereoselective synthesis of (Z)-5-alkenylazolidin-2-ones when starting from 4-monosubstituted 2,3-allenyl amines [53].

Scheme 16. Synthesis of 5-vinyl-2-oxazolidinones 15 from 2,3-allenyl amines and aryl iodides.

Conjugate dienes are also reactive toward carbon dioxide under palladium catalysis. Following the pioneering studies performed by the groups of Inoue [54,55] and Musco [56,57], in 1983 Behr and coworkers reported the reaction of 1,3-butadiene with CO₂ carried out in the presence of Pd(acac)₂ as the palladium source (0.18%) and 1,3-Pr₃P as ligand, in acetonitrile at 90 °C, to give 3-ethylidene-6-vinyltetrahydro-2H-pyran-2-one (or 2-ethylidene-6-hepten-5-olide, EVL) 16 in 38% isolated yield and a TON (Turnover Number) of ca. 310 mol of product per mol of palladium used (Scheme 17) [58,59]. Interestingly, this 6-membered lactone could be isomerized into the corresponding 5-membered one [3-ethyl-5-propylidenefuran-2(5H)-one, 17% GLC yield] under the same reaction conditions, but with a higher catalyst loading (1.19%) [59]. EVL is a useful precursor for the preparation of different high value added products [60–64], including polymers [62–64], such as high molecular weight polymers with a carbon dioxide content of 33 mol%, obtained by the δ-lactone free-radical polymerization [64]. Mechanistically, the telomerization process leading to EVL was believed to occur through the formation of a bis-π-allylpalladium complex I from the reaction between butadiene and Pd(0), followed by CO₂ insertion and cyclization with reductive elimination of Pd(0) (Scheme 17).

Scheme 17. Synthesis of 2-ethylidene-6-hepten-5-olide 16 (EVL) from 1,3-butadiene.

The process was later studied by Dinjus and Leitner [65], among others [66–69], who were able for the first time to isolate and characterize by NMR the mixture of isomeric lactones [6-(prop-1-en-2-yl)-3-(propan-2-ylidene)tetrahydro-2H-pyran-2-one and 6-methyl-3-
(propan-2-ylidene)-6-vinyltetrahydro-2H-pyran-2-one) obtained from isoprene [65]. These studies evidenced the importance of the use of a hindered phosphine ligand as well as of a nitrile solvent for the success of the reaction.

More recently, various catalytic systems have been developed to perform the telomerization of butadiene with CO$_2$ to give lactones, including Pd(OAc)$_2$ in the presence of ferrocenylphosphine ligands, such as 1,1′-bis(diisopropylphosphinoferroocene (disopf) [70], Pd(acac)$_2$/PC$_3$ [62,71], Pd(acac)$_2$/PPh$_3$ [64], Pd(dbazu)$_2$/4-(2-(diphenylphosphino)phenyl)morpholine [72], Pd(acac)$_2$/TBAAC (TBAAC = tetrabutylammonium acetate) [63,73], Pd(dbazu)$_2$/TOMPP (TOMPP = tris-(o-methoxynaphthyl)phosphine) [74], and Pd(OAc)$_2$/TPMPP/H$_2$Q/DIPEA (TPMPP = tris-(p-methoxyphenyl)phosphine, H$_2$Q = p-hydroquinone, DIPEA = N,N-diisopropylethylamine) [75]. In particular, using the last catalytic system, EVL was obtained in 96% selectivity and with an unprecedented TON of ca. 4500, by performing the reaction in MeCN at 70 °C for 5 h [75].

3. Palladium-Catalyzed Incorporation of Carbon Dioxide into Acetylenic Substrates

Acetylenic substrates have been reported to undergo several important carboxylation processes catalyzed by palladium, with formation of high value added compounds.

In 1986, Utimoto and coworkers reported the Pd(II)-catalyzed reaction of lithium 2-alkynyl carbonates (obtained from the reaction between lithium alkyn-1-olates with CO$_2$) with allylic chlorides to give 4-(but-3-en-1-ylidene)-1,3-dioxolan-2-ones 17 (Scheme 18) [76]. The synthetic transformation was carried out in a one-pot, two-step fashion, by allowing ynlolate to react with CO$_2$ first (in THF at −78 °C) and then adding the allyl chloride together with the catalyst PdCl$_2$(MeCN)$_2$ at the same temperature followed by stirring at 0 °C for 4 h, as shown in Scheme 18.

![Scheme 18](image)

(R$^1$ = H, alkyl, Ph, SiMe$_3$, SiMe$_2$Ph; R$^2$, R$^3$, R$^4$, R$^5$, R$^6$ = H, Me)

Later on, Inoue and coworkers reported the Pd(0)-catalyzed reaction between sodium 2-alkyn-1-olates bearing a terminal triple bond, aryl halides, and CO$_2$ to give cyclic carbonates 18 [((E)-4-(arylmethylene)-1,3-dioxolan-2-ones], as shown in Scheme 19 [77]. Reactions were carried out under 10 atm of CO$_2$, in THF at 100 °C and in the presence of 2 mol% of Pd(PPh$_3$)$_4$. In this process, the initial oxidative addition of the aryl halide to Pd(0) leads to an Ar–Pd–X complex, which electrophilically activates the triple bond toward the anti
5-exo-dig intramolecular nucleophilic attack by the carbonate anion I formed by the reaction between the ynolate and CO2 (Scheme 19).

\[
\begin{align*}
\text{ArX} + \text{Pd}(0) & \rightarrow \text{Ar-Pd-X} \\
\text{Ar} & + \text{Pd} + \text{CO}_2 + \text{Na} \rightarrow \text{Ar-Pd} + \text{CO}_2
\end{align*}
\]

Scheme 19. Synthesis of (E)-4-(arylmethylene)-1,3-dioxolan-2-ones 18 from sodium 2-alkyn-1-olates and aryl halides.

2-Ynolates can also be formed in situ starting by deprotonation of propargyl alcohols in the presence of a suitable base. For example, recently a variety of propargyl alcohols with the triple bond substituted with an aryl group were converted into 5-(diaryl methylene)-1,3-dioxolan-2-ones 19 by their Pd(0)-catalyzed reaction with aryl halides and CO2 (1 atm), carried out in the presence of Pd3(dba)3 as catalyst and tBuOLi as the base (Scheme 20) [78]. Interestingly, with substrates bearing a terminal triple bond, a sequential Sonogashira coupling–carboxylation process took place, as exemplified in Scheme 20 for the case of the reaction of 2-methylbut-3-yn-2-ol with PhI (3 equiv) and CO2. The reaction, carried out in the presence of 5 mol% of PdCl2(PPh3)2 as the catalyst precursor, Cul (10 mol%) as cocatalyst, and tBuOLi as base (3 equiv), led to formation of 5-(diphenylmethylen)-4,4-dimethyl-1,3-dioxolan-2-one 20 in 55% yield (Scheme 20).

\[
\begin{align*}
\text{Ar}^1 & + \text{Ar}^2 + \text{CO}_2 + \text{Me} + \text{Na} \rightarrow \text{Ar}^1\text{Ar}^2 \text{CO}_2
\end{align*}
\]

(R1 = H, alkyl, Ph; R2 = H, alkyl)

Scheme 20. Synthesis of 5-(diaryl methylene)-1,3-dioxolan-2-ones 19 and 20 from propargyl alcohols and aryl halides.

Polymeric materials can be obtained starting from bis(propargyl alcohol)s and aryl dihalides. Thus, linear and hyperbranched five-membered cyclic carbonate-based polymers 21 with high weight-average molecular weights (up to 42,500, 96% yield) were recently produced by allowing to react bis(propargyl alcohol) monomers and aryl dihalide monomers with CO2 (1 atm) in DMF in the presence of Pd(OAc)2 as catalyst precursor and tBuOLi as the base (Scheme 21) [79].
Scheme 21. Formation of five-membered cyclic carbonate-based polymers 21 from bis(propargylic alcohol)s and aryl dihalides.

With propargylic substrates bearing a potential leaving group, Pd-catalyzed CO$_2$ sequential elimination–fixation may occur through the formation of π-propargylpalladium species, in a similar way as seen in Section 2 for allylic carbonates (Schemes 6 and 7) [80]. Thus, in 2001, Yoshida and Hihara reported the synthesis of aryloxyvinyl-substituted 5-membered cyclic carbonates 22 by the reaction of 4-hydroxy-2-yn-1-yl methyl carbonates with phenols, carried out in the presence of Pd$_2$(dba)$_3$ and dppe in dioxane at 25–50 °C (Scheme 22) [81]. Higher product yields were obtained by performing the reaction under 1 atm of CO$_2$ [81–83]. The reaction was also shown to be enantioselective (ees up to 93%) in the presence of the nonracemic ligand (S)-BINAP [82] and enantiospecific (with chirality transfer) when starting from nonracemic substrates [83]. The process begins with the reaction between the substrate and Pd(0) to give carbon dioxide and π-propargylpalladium methoxide complex I. The latter then undergoes nucleophilic attack by phenol leading to a π-allylpalladium intermediate II, from which the final product is formed by attack to CO$_2$ followed by intramolecular nucleophilic attack of the ensuing carbonate to the π-allylpalladium moiety (Scheme 22).

Scheme 22. Synthesis of 4-(1-aryloxyvinyl)-1,3-dioxolan-2-ones 22 from 4-hydroxy-2-yn-1-yl methyl carbonates and phenols.

More recently, some propargylic epoxides with internal triple bond (trans-1-ethynyl-7-oxabicyclo[4.1.0]heptanes, in particular) were also used as substrates under similar conditions, with the addition of 3A molecular sieves (MS) (presumably to avoid substrate...
ring opening by water) and under 1 atm of CO₂ (Scheme 23) [84]. The reaction, leading to 2-substituted (1-aryloxyvinyl)hexahydrobenzo[Δ][1,3]dioxol-2-ones 23 in modest to good yields, took place through the same kind of mechanistic route seen above for propargylic carbonates (Scheme 22), the key π-propargylpalladium zwitterionic complex I being this time formed by Pd(0)-promoted epoxide ring opening through an anti Sn2'-type attack (Scheme 23).

![Scheme 23. Synthesis of 2-substituted (1-aryloxyvinyl)hexahydrobenzo[Δ][1,3]dioxol-2-ones 23 from trans-1-ethynyl-7-oxabicyclo[4.1.0]heptanes and phenols.](image)

Propargyl amines are excellent substrates for the Pd-catalyzed CO₂ incorporation to give high value added oxazolidinone derivatives. In 1997, our research group reported the first example of catalytic sequential incorporation of both carbon oxides (carbon dioxide and carbon monoxide) into an organic substrate, α,α'-disubstituted propargylamines in particular [85]. The process was catalyzed by Pd(II) and took place in the presence of PdI₂ (1 mol%), KI, MeOH (also used as solvent) at 50 °C for 25–65 h, under 50 atm of a 8:1:1 mixture of CO₂-CO-air, to give mixtures of 5-(methoxycarbonylmethylene)oxazolidin-2-ones 24 (with Z configuration of the double bond) and 24' (with E configuration around the exocyclic double bond) in 80–90% total yields (Z/E ratio from 2:1 to 3:1) (Scheme 24) [85,86]. Overall, the reaction corresponded to an oxidative carbonylation [87–99] of the carbamate species initially formed by nitrogen attack to CO₂, with oxygen (from air) as the external oxidant and with formation of water as benign coproduct. More specifically, the anionic carbamate I (formed from the reaction between the propargylamine substrate and CO₂) led to the main product, (Z)-5-(methoxycarbonylmethylene)oxazolidin-2-one 24, through the formation of a palladium carbamate complex II, followed by intramolecular syn 5-exo-dig insertion of the triple bond to give III, CO insertion to IV, and nucleophilic displacement by MeOH (Scheme 24, path a) [85,86]. On the other hand, intermediate I could also undergo anti 5-exo-dig nucleophilic attack of the anionic carbamate moiety to the triple bond coordinated to Pd(II), leading to an E-vinylpalladium complex V. Carbon monoxide insertion then took place, with formation of an E-acylpalladium intermediate VI, from which the final (E)-5-(methoxycarbonylmethylene)oxazolidin-2-one 24' was formed by nucleophilic displacement by MeOH (Scheme 24, path b). In either case, Pd(0) was formed together with the organic products. The overall process became catalytic thanks to a very efficient reoxidation of Pd(0) to Pd(II), involving the initial oxidation of 2 mol of HI (also formed during the reaction) by oxygen (from air) to produce iodine, followed by the oxidative addition of I₂ to Pd(0) to give back PdI₂ (Scheme 24) [100,101].
More recently, it was reported the use of an indenediide palladium complex as efficient catalyst for promoting this kind of transformation with a variety of differently substituted substrates (including propargyl amines bearing an internal triple bond), under mild conditions (0.5 mol%) (Scheme 26) [103]. The Pd-catalyzed incorporation of CO alone (without CO) into propargylic amines has also been reported. Thus, in 2002, Shi and Shen published the Pd(II)-catalyzed carboxylation of these substrates under 40 Kg/cm2 of CO2 to give methyleneoxazolidinones 25, using Pd(OAc)2 as catalyst precursor, in toluene as the solvent at 50 °C for 48 h (Scheme 25) [102]. Products were possibly formed through mechanistic pathways similar to those seen before in Scheme 24, as shown in Scheme 25.

Scheme 24. Synthesis of 5-(methoxycarbonylmethylene)oxazolidin-2-ones 24 and 24 from propargyl amines.

This sequential carboxylation–oxidative alkoxy carbonylation of propargyl amines to 5-(methoxycarbonylmethylene)oxazolidin-2-ones still today represents the only example reported in the literature of Pd(II)-catalyzed incorporation of both CO2 and CO into an organic substrate.

The Pd-catalyzed incorporation of CO2 alone (without CO) into propargylic amines has also been reported. Thus, in 2002, Shi and Shen published the Pd(II)-catalyzed carboxylation of these substrates under 40 Kg/cm2 of CO2 to give methyleneoxazolidinones 25, using Pd(OAc)2 as catalyst precursor, in toluene as the solvent at 50 °C for 48 h (Scheme 25) [102]. Products were possibly formed through mechanistic pathways similar to those seen before in Scheme 24, as shown in Scheme 25.

Scheme 25. Synthesis of 5-methyleneoxazolidin-2-ones 25 from propargyl amines.

More recently, it was reported the use of an indenediide palladium complex as efficient catalyst for promoting this kind of transformation with a variety of differently substituted substrates (including propargyl amines bearing an internal triple bond), under mild cond-
tions (0.5–1 bar of CO$_2$, 40–80 °C in DMSO as the solvent), although with a higher catalyst loading (1–5 mol%) (Scheme 26) [103]. The Z configuration around the exocyclic double bond, observed for the 5-alkyldeneoxazolidin-2-ones 26 obtained from propargyl amines with internal triple bond, was compatible with the anti 5-exo-dig cyclization pathway, as shown in Scheme 26. Detailed DFT investigations allowed identifying the cyclization step as the rate-determining step of the process.

![Scheme 26. Synthesis of 5-alkyldeneoxazolidin-2-ones 26 from propargyl amines.](image)

Carboxylation of propargyl amines in the presence of aryl halides under the catalysis of Pd(0), with formation of 5-arylideneoxazolidin-2-ones 27, is also possible, as shown in Scheme 27 [104]. The process starts with the oxidative addition of the aryl iodide to Pd(0) [formed in situ from PdCl$_2$(dppe)] to give an Ar–Pd–I complex. On the other hand, a carbamate intermediate is also formed by the reaction of the propargyl amine with CO$_2$ in the presence of t-BuONa as base. Coordination of the triple bond of I to the Pd(II) center of the ArPdI species then takes place, followed by 5-exo-dig cyclization and reductive elimination to give the final product 27 with regeneration of Pd(0).

![Scheme 27. Synthesis of 5-arylideneoxazolidin-2-ones 27 from propargyl amines and aryl iodides.](image)
In a similar manner, more recently 5-arylideneoxazolidine-2,4-diones 28 were synthesized starting from propargylic amides, aryl halides, and CO$_2$, in the presence of PdCl$_2$(PPh$_3$)$_2$ as the catalytic precursor, Cul as cocatalyst, and potassium carbonate as base (Scheme 28) [105]. The role of Cul was believed to be related to the possible stabilization of the carbamate intermediate I (by chelation of the amide carbonyl and the carboxylate group, leading to complex II), which avoids protonolysis, leading to oxazolidinones not incorporating the aryl moiety.

Scheme 28. Synthesis of 5-arylideneoxazolidine-2,4-diones 28 from propargyl amides and aryl iodides.

4. Palladium-Catalyzed Incorporation of Carbon Dioxide into Other Substrates

Under suitable conditions, aryl halides and triflates can undergo palladium-catalyzed carboxylation with formation of important compounds.

In 2017, the groups of Maes and Beller reported the Pd(0)-catalyzed reaction of 2-bromoanilines with CO$_2$ and isocyanides to give quinazoline-1,4(1H,3H)-diones 29 [106]. Reactions were performed in the presence of Pd(OAc)$_2$ as the catalyst precursor, in the presence of BuPdAd$_2$ (Ad = adamantly) as ligand and Cs$_2$CO$_3$ as base, in dioxane as the solvent at 80 °C and under 10 bar of CO$_2$ (Scheme 29). In the simplified version of the mechanism, oxidative addition of the Ar–Br bond to Pd(0) takes place, followed by insertion of the isocyanide. The reaction of the amino group with CO$_2$ in the presence of the base then leads to a palladium carbamate intermediate I, which undergoes reductive elimination to yield Pd(0) and a 4-imino-1,4-dihydro-2H-benzo[d][1,3]oxazin-2-one intermediate II, from which the final product is obtained by base-promoted rearrangement (Scheme 29).

Scheme 29. Synthesis of quinazoline-1,4(1H,3H)-diones 29 from 2-bromoanilines and isocyanides.
In the same year (2017), independently, the group of Wang and Ji published exactly the same transformation from 2-iodoanilines under atmospheric pressure of carbon dioxide, using PdCl$_2$ in the presence of PPh$_3$ as the catalyst precursor and DBU as the base, in MeCN at 80 °C (Scheme 30) [107]. Additionally, in 2018 Zhang and coworkers reported the use of both 2-bromo- and 2-idoanilines using catalytic amounts of Pd(OAc)$_2$ in the presence of PPh$_3$ as ligand and CsF as base, under 2 MPa of CO$_2$, in DMSO at 90 °C (Scheme 31) [108].

\[
\begin{align*}
\text{R}^1 \text{I} & + \text{R}^2 \text{NC} + \text{CO}_2 \\
& \xrightarrow{\text{PdCl}_2 (10 \text{ mol\%})} \text{R}^1 \text{N} \text{R}^2
\end{align*}
\]

\[
\text{PPh}_3 (20 \text{ mol\%})
\]

\[
\text{DBU (2 equiv)}
\]

\[
\text{CO}_2 (1 \text{ atm})
\]

\[
\text{MeCN, 80 °C, 12 h (40-96\%)}
\]

(R$^1$ = H, Me, OMe, F, Cl, Br, CF$_3$, NO$_2$; R$^2$ = alkyl)

**Scheme 30.** Synthesis of quinazoline-1,4(1H,3H)-diones from 2-iodoanilines and isocyanides.

\[
\begin{align*}
\text{R} \text{X} & + \text{t-BuNC} + \text{CO}_2 \\
& \xrightarrow{\text{Pd(OAc)}_2 (10 \text{ mol\%})} \text{R} \text{N} \text{Bu}
\end{align*}
\]

\[
\text{PPh}_3 (20 \text{ mol\%})
\]

\[
\text{CsF (2 equiv)}
\]

\[
\text{CO}_2 (2 \text{ MPa})
\]

\[
\text{DMSO, 90 °C, 12 h (14-85\%)}
\]

(R = H, Me, F, Cl, Br, CN, CF$_3$; X = Br, I)

**Scheme 31.** Synthesis of quinazoline-1,4(1H,3H)-diones from 2-haloanilines and tert-butyl isocyanide.

Interestingly, very recently this kind of reactivity has been exploited for the synthesis of new heterocyclic polymers 30 with self-assembly and sensing properties, starting from bis(2-iodoaniline) and diisocyanide monomers, using PdCl$_2$ and PPh$_3$ as the catalyst precursor, under 1 atm of CO$_2$, in DMA at 80 °C for 18 h (Scheme 32) [109].

\[
\begin{align*}
\text{H}_2 \text{N} & + \text{CN} \text{-dione} + \text{CO}_2 \\
& \xrightarrow{\text{PdCl}_2 (15 \text{ mol\%})} \text{N} \text{R}^1 \text{R}^2
\end{align*}
\]

\[
\text{PPh}_3 (30 \text{ mol\%})
\]

\[
\text{DBU (3 equiv)}
\]

\[
\text{CO}_2 (1 \text{ atm})
\]

\[
\text{DMA, 80 °C, 18 h}
\]

**Scheme 32.** Synthesis of heterocyclic polymers 30 from bis(2-iodoaniline)s and diisocyanides.

Palladium-catalyzed incorporation of CO and CO$_2$ into 2-idoanilines to give isatoic anhydrides 31 has also been reported [110]. Reactions were carried out in THF at 60 °C under 1 MPa of CO$_2$ and 0.5 MPa of CO, in the presence of Pd(PPh$_3$)$_4$ as catalyst and AcOCCs as base (Scheme 33). Mechanistically, the process is similar to that seen in Scheme 29, with CO in place of the isocyanide (and without the final rearrangement step) (Scheme 33).
In 2009, Correa and Martín reported the first example of palladium-catalyzed carboxylation of aryl bromides to benzoic acids [111]. Reactions were carried out with Pd(OAc)$_2$ as the catalyst precursor in the presence of tBuXPhos as ligand (tBuXPhos = di-tert-butyl(2',4',6'-triisopropyl-[1,1'-biphenyl]-2-yl)phosphine) and 2 equiv of Et$_2$Zn as reductant, in DMA/hexanes at 40 °C and under 10 atm of CO$_2$ (Scheme 34). The proposed mechanism involves the oxidative addition of the aryl bromide to the in situ formed Pd(0), followed by carbon dioxide insertion and transmetallation with Et$_2$Zn to give a zinc carboxylate I and an Et–Pd–Br species. Reductive elimination from the latter then regenerates Pd(0), while the benzoic acid product is obtained from zinc carboxylate following acidic work-up (Scheme 34).

More recently, the first visible-light driven carboxylation of aryl halides (chlorides or bromides) to give methyl benzoates has also been reported [110]. Reactions were carried out in THF at 60 °C and 2,2'-dipyridine (dtbpy) as a photoredox catalyst and 0.5 MPa of CO, in the presence of Pd(PPh$_3$)$_3$ as catalyst and 2 equiv of Et$_2$Zn (Scheme 35). This method avoids the use of metallic reductants (such as Et$_2$Zn, seen before, Scheme 34) and is also compatible with aryl chlorides, unreactive under the conditions of Scheme 34. It is worth noting that the carboxylation of aryl halides with carbon dioxide can also be catalyzed by first-row trans-
tion metals, including copper [113], nickel [114], and cobalt [115] catalysts. However, only palladium catalysis seems to be compatible with visible light-promoted conditions so far. A possible mechanism starts with the oxidative addition of the aryl halide to Pd(0), followed by reversible CO$_2$ insertion. A single-electron reduction by an Ir(II) complex then takes place, with formation of a Pd(I) carboxylate species I and an Ir(III) species. The Pd(I) carboxylate finally undergoes a second single-electron reduction to give the aryl carboxylate with regeneration of Pd(0). The Ir(III) species is reconverted into Ir(II) by photoexcitation followed by the reaction of the excited Ir(III)$^*$ species with DIPEA (Scheme 35).

**Scheme 35. Synthesis of methyl benzoates 33 from aryl halides.**

In a similar way, recently aryl triflates have been converted into benzoic acids 32 by Pd(0)-catalyzed, visible light-promoted carboxylation, carried out in the presence of Pd(OAc)$_2$ as the catalyst precursor, DavePhos as ligand [DavePhos = 2-dicyclohexylphosphino-2′-((N,N-dimethylamino)biphenyl] and Ir(ppy)$_2$(dtbpy)PF$_6$ as photoredox cocatalyst (ppy = polypyrrole) [116]. Reactions were carried out under conditions similar to those seen above for aryl halides, namely, at r.t. and atmospheric pressure of CO$_2$ in DMA as the solvent and in the presence of Cs$_2$CO$_3$ as base and DIPEA as electron donor (Scheme 36).

**Scheme 36. Synthesis of benzoic acids 32 from aryl triflates.**

5. Conclusions

The versatility of palladium-based catalysts has been successfully exploited also in the efficient conversion of carbon dioxide into high value added organic molecules of applicative and pharmacological interest. Many different important Pd-catalyzed carboxylation processes have been developed and discussed in this review, mainly based on Pd(0) catalysis, although important Pd(II)-catalyzed reactions have also been reported. Particularly important results have been achieved in the Pd(0)-promoted CO$_2$ incorporation into small rings (such as suitably functionalized epoxides and aziridines) as well as into suitably functionalized alkenes, allenes, or alkynes, to give highly important heterocyclic derivatives, such as cyclic carbonates, oxazolidinones, etc. Under Pd(II) catalysis, particularly important results have been achieved with propargyl amines as substrates, with formation
of oxazolidinones, which could also incorporate an exocyclic estereal function working in the presence of CO together with CO$_2$ under appropriate conditions.

On this grounds, it is expected that in the future palladium will play a major role in CO$_2$ utilization and incorporation into suitable substrates, possibly in the presence of other promoting species (either metal-based or organo-based) as cocatalyst(s), which will allow us to achieve more demanding processes for the direct and selective synthesis of complex molecular architectures.

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