Transition-Metal-Catalyzed Carboxylation of Organic Halides and Their Surrogates with Carbon Dioxide

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Abstract Carbon dioxide is not only an essential component of 'greenhouse gases', but also an abundant, renewable C1 feedstock in organic synthesis. The catalytic incorporation of carbon dioxide into value-added chemicals to produce carboxylic acids has received enormous attention. This review summarizes recent developments in the transitionmetal-catalyzed carboxylation of organic halides and their surrogates, such as aryl, vinyl, and alkyl halides and pseudohalides.

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Key words carbon dioxide, carboxylic acids, carboxylation, electrophiles, halides

1 Introduction

The continuous increase of carbon dioxide concentration in the atmosphere has potentially caused the rise of atmospheric temperature and abnormal changes in the global climate.¹ Obviously, the control of CO₂ emissions and the development of efficient carbon capture systems are in high demand. Carbon dioxide is not only an essential component of 'greenhouse gases', but also an abundant and renewable C1 feedstock in organic synthesis.² Therefore, there is great interest in transforming carbon dioxide into useful chemicals, from an environment-protection point of view. Due to



the thermodynamically stable and/or kinetically inert of CO₂, the activation and utilization of CO₂ is still problematic. Most transformations of CO₂ require highly reactive substrates and/or severe reaction conditions. In the case of C–C bond formation with CO₂, the use of carbon nucleophiles is limited to phenolates and strongly nucleophilic organolithium, as well as Grignard reagents.³ On the other hand, highly reactive substrates such as epoxides and aziridines are used to couple with CO₂ to generate C–O or C–N bonds.⁴ In this article, recent developments for the transition-metal-catalyzed carboxylation of electrophiles, such as aryl, vinyl, benzyl, allyl, propargyl, alkyl and halides and pseudohalides will be highlighted (Figure 1). The carboxylation of



Figure 1 The representative examples of carboxylation reactions in this review

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Tian-Sheng Mei received his B.Sc. in chemistry in 2001 from Lanzhou University for research into the total synthesis of terpene natural products under the supervision of Prof. Yu-Lin Li. In 2005 he moved to the group of Prof. Jin-Quan Yu at Brandeis University, where he received his M.Sc. He subsequently relocated to the Scripps Research Institute, where he obtained his Ph.D. in 2012 for research into Pd-catalyzed C–H functionalization under Prof. Jin-Quan Yu. He joined the research group of Prof. Matt Sigman at University of Utah, where his postdoctoral research involves the development of intermolecular asymmetric Heck reactions. In 2014, he then began his independent career at State Key Laboratory of Organometallic Chemistry, Shanghai Institute of Organic Chemistry (SIOC). His group studies carbon dioxide chemistry and organometallic electrochemistry.

alkenes and alkynes as well as organometallics, such as organotin, organozinc, and organoboron reagents, with $\rm CO_2$ have been well documented and will not be discussed further in this review.⁵

2 Carboxylation of Aryl Halides and Pseudohalides

The carboxylation of arylzinc and arylboronic esters with CO_2 has been investigated intensively, due to the compatibility of various functionalities that were not tolerated with Grignard reagents. However as these compounds were derived from the corresponding aryl halides, the direct carboxvlation of the arvl halides is a more straightforward transformation. The stoichiometric carboxylation of Ni-aryl complexes with CO₂ has been studied intensively. For example, the insertion of CO_2 into the Ni-arvl carbon bond of **1** and 2 delivers corresponding nickelalactones 1a and 2a, respectively (Scheme 1).⁶ The Ni(0)-mediated carboxylation of arvl halides **3** with CO₂ was demonstrated by Yamamoto. Osakada, and Sato. Oxidative addition of the aryl halide 3 to $Ni(cod)_2$ in the presence of 2,2'-bipyridine gives NiX(Ph)(bpy) 4, which reacts with CO₂ to deliver the carboxylation products 5 (Scheme 1).⁷



CO2 (1 atm)

78 °C

P(n-Bu)₃

1

-P(*n*-Bu)₃

Scheme 1 Ni-mediated carboxylation of aryl halides

Early examples of the Ni-catalyzed carboxylation of aryl halides were reported as electrochemical processes. For instance, Perichon, Fauvarque, and co-workers described the electroreductive carboxylation of aryl halides **3** with CO₂ in

P(n-Bu)₃

. P(*n*-Bu)₃

1a

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the presence of nickel catalyst.⁸ The proposed mechanism is shown in Scheme 2. Oxidative addition of aryl bromide **3** (X = Br) to Ni(0)(dppe) gives ArNi^{II}Br(dppe), which undergoes one-electron reduction to deliver a Ni(I) complex. Carboxylation of the arylnickel(I) species and one-electron reduction closes the cycle by regeneration of Ni(0) and formation of arenecarboxylate (Scheme 2). On the basis of the kinetic analysis of the CO₂ insertion step, a Ni(III) intermediate is also proposed prior to the formation of ArCO₂Ni(dppe).⁹



Scheme 2 Ni-catalyzed carboxylation of aryl bromide via electrochemical reduction

Similarly, Torii, Fauvarque, and co-workers disclosed an efficient Pd-catalyzed electroreductive carboxylation of aryl halides with CO_2 (Scheme 3).¹⁰ Both aryl iodides **3** (X = I) and aryl bromides **3** (X = Br) are effective, however aryl chlorides did not give the corresponding products. It is noteworthy that the formation of arenecarboxylate was not competitive with the formation of biaryl, which is the by-product for the metal-free electroreductive carboxylation.¹¹

The transition-metal-catalyzed electroreductive carboxylation of aryl halides with CO_2 is a promising tool for the preparation of arenecarboxylic acids.¹² However the reaction scope is quite restricted. In 2009, Correa and Martín reported a Pd-catalyzed carboxylation reaction of aryl bromides **6** using a substituted biphenyl monophosphine ligand **L**₁ (*t*-Bu-Xphos) under 10 atm of CO_2 .¹³ The insertion of CO_2 into the Pd–aryl σ -bond is suggested in the proposed mechanism. Diethylzinc behaves as the reducing agent to regenerate Pd(0) and zinc carboxylates are formed (Scheme 4). In 2012, Tsuji and co-workers described the Ni-catalyzed carboxylation of aryl chlorides **3** (X = Cl) under 1 atm of CO_2 using Mn powder as a reducing agent.¹⁴ The proposed





Scheme 3 Pd-catalyzed carboxylation of aryl halides

mechanism involves an oxidative addition of the aryl chlorides to Ni(0), formed by reducing Ni(II) with Mn. The resulting Ni(II) intermediate is reduced to a Ni(I) intermediate, which reacts with CO_2 to give the product (Scheme 5).



Scheme 4 Pd-catalyzed carboxylation of aryl halides

Copper catalysts have been used in the carboxylation of arylboronates with CO_2 , and an aryl-copper species is suggested as a key intermediate for the reaction. In 2013, Tran-Vu and Daugulis reported the Cu-catalyzed carboxylation of aryl iodides **7** under 1 atm of CO_2 .¹⁵ The reaction is compatible with various functional groups such as ester, bromide, chloride, fluoride, ether, amino, hydroxy, and carbonyl. The carboxylation of aryl–Cu species is suggested to be rate-limiting step and the mechanism is likely to involve copper clusters (Scheme 6).

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Scheme 5 Ni-catalyzed carboxylation of aryl halides



Besides aryl halides, aryl pseudohalides are suitable electrophiles for carboxylation reactions. For instance, Martín and co-workers demonstrated the Ni(II)-catalyzed carboxylation of $C(sp^2)$ –O bonds with CO_2 , and it is necessary that the C–O bonds are pre-activated as esters, e.g. **8**, derived from cheap alcohols.¹⁶ The reaction mechanism is similar to C–halides carboxylation using Mn as reducing reagent (Scheme 7). These carboxylation reactions provide alternative protocols for the preparation of arenecarboxylic acids with the advantage of functional group tolerance compared with the classic carboxylation of Grignard reagents. Obviously, the development of novel carboxylation reactions to avoid the use of stoichiometric amounts of metals (Mn or Zn) or zinc agents as reducing agents is in high demand.



Scheme 7 Ni-catalyzed carboxylation of aryl pivalates

3 Carboxylation of Vinyl Halides and Pseudohalides

The carboxylation of a vinyl bromide **10** was achieved through an electroreductive process in the presence of palladium catalyst (Scheme 8).¹⁰ Interestingly, this carboxylation gives dicarboxylic acid **11**, which is formed via the primary product **10a**. Electrolysis of carboxylate **10a** gives the dicarboxylic acid **11** in 61% yield. In 1997, Juland and Négri reported the Pd-catalyzed carboxylation of vinyl triflates **12** with CO₂ (Scheme 9).¹⁷





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In 2015, Tsuji and co-workers¹⁸ reported a cobalt-catalyzed reductive carboxylation reaction. In this work, various alkenyl triflates **14** were converted into α , β -unsaturated carboxylic acids **15** under mild conditions (Scheme 10). In addition, a range of hindered aryl triflates substituted in the 2-aryl position were smoothly carboxylated.



4 Carboxylation of Benzyl Halides and Pseudohalides

The adduct of Co(salen) and CO_2 was described by Fachinetti and Floriani in 1974.^{19a} In 1985, Perichon and coworkers demonstrated the Co-catalyzed reductive carboxylation of benzyl chloride **16** with CO_2 via an electrochemical process, although the reaction mechanism was not explored (Scheme 11).^{19b}





In 2013, the Martin group reported the Ni-catalyzed carboxylation of benzyl chlorides **16** with CO₂ (Scheme 12);²⁰ the reaction tolerated various functional groups. Interestingly, with slightly modified reaction conditions, the carboxylation of secondary alkyl bromides **19** was achieved (Scheme 13).²⁰ The proposed mechanism suggests that a Ni¹ intermediate may be crucial in the catalytic cycle and MgCl₂ promotes the carboxylation of benzyl chloride with CO₂ by stabilizing the Ni–CO₂ adduct and accelerating the CO₂ insertion (Scheme 14).^{20,21}



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In 2014, the Martin group also demonstrated the carboxylation of benzylic C(sp³)–O bonds via a similar pathway (Scheme 15).¹⁶ Notably, the carboxylation of secondary benzyl-type derivatives (e.g., 18f.h.i) was also effective. However, the protocol is limited to π -extended systems; simple phenyl-containing compounds are not effective. Taking advantage of hemilabile directing group,²² the Martin group elegantly developed the efficient carboxylation protocol with simple benzyl esters 20 (Scheme 16).¹⁶ Furthermore, the Martin group demonstrated that ammonium salts 21 could be used as benzyl electrophiles for carboxylation (Scheme 17).²³ Interestingly, this reaction was insensitive to electronic changes on the arene and suitable for non-extended π-systems. Most striking, secondary benzyl ammonium salts 22 possessing α -hydrogen atoms were successfully carboxylated. The dimerization and α -hydride elimination pathways were avoided in this protocol (Scheme 18).²³











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Scheme 17 Ni-catalyzed carboxylation of primary ammonium salts

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In 2015, He and co-workers reported the Pd-catalyzed carboxylation of benzyl chlorides **16** with CO_2 (Scheme 19).²⁴ The reaction afforded the corresponding phenylacetic acids **17** in combination with Mn powder as a reducing reagent and MgCl₂ as an indispensable additive.

Lu and co-workers reported the asymmetric electrocarboxylation of 1-phenylethyl chloride (**16b**) with CO_2 in the presence of Co catalyst (Scheme 20).²⁵ Although the yield and the ee values are moderate, this elegant study provides an alternative method for the synthesis of optically active carboxylic acids.



Scheme 20 Co-catalyzed asymmetric electrocarboxylation of 1phenylethyl chloride (GC = glassy carbon)

5 Carboxylation of Allyl Halides and Pseudohalides

In 1976, Inoue and co-workers described the carboxylation of allylic Pd species with CO_2 .²⁶ In the 1980s, Perichon^{19b} and Fauvarque¹⁰ described the electroreductive carboxylation of allylic substrates with CO_2 in the presence of cobalt and palladium catalysts, respectively (Scheme 21). Unfortunately, regioselectivity is not achieved under these conditions.

In 2014, the Martin group demonstrated the Ni-catalyzed carboxylation of allyl esters with CO_2 (Scheme 22).²⁷



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Scheme 21 Electroreductive carboxylation of allylic substrates with CO₂ in the presence of cobalt and palladium catalysts

The regioselectivity is highly controlled by the ligand and both carboxylic acid products were achieved in a highly selective manner with 1,10-phenanthroline L_2 or quaterpyridine L_5 ligands.

Carboxylation with an allylic alcohol without pre-activation is a highly attractive transformation from the perspective of step-economy. Mita, Sato, and Higuchi elegantly demonstrated the Pd-catalyzed carboxylation of allylic alcohols **28** and **29** with CO₂ using ZnEt₂ as the reducing agent (Scheme 23).²⁸ The allylic alcohol is likely activated by the Lewis acid ZnEt₂ or by carbonate formation with CO_2 .²⁹ This carboxylation is highly regioselective and gives predominantly branched carboxylic acid. The proposed mechanism is shown in Scheme 23.

In 2017, the Martin group elegantly demonstrated the switchable site-selective Ni catalyzed carboxylation of allylic alcohols with CO₂. The regiodivergency can be modulated by the type of ligand employed (Scheme 24).²⁹

Also in 2017, Mei and co-workers developed an efficient Ni-catalyzed reductive carboxylation of allylic alcohols with CO_2 , providing linear β , γ -unsaturated carboxylic acids **24** as the sole regioisomer with generally high *E*/*Z* stereoselectivity (Scheme 25).³⁰ In addition, the carboxylic acids were generated from propargylic alcohols via hydrogenation to give allylic alcohol intermediates, followed by carboxylation. A preliminary mechanistic investigation suggests that





the hydrogenation step is made possible by a Ni-hydride intermediate produced by a hydrogen atom transfer from water.

6 Carboxylation of Propargyl Halides and Pseudohalides

In 2014, Tsuji, Fujihara and co-workers reported the Cocatalyzed carboxylation of propargyl acetates **32** with CO_2 at room temperature using Mn powder as a reducing agent (Scheme 26).³¹ The proposed mechanism suggests a Co(II) **C** as a possible intermediate that reacts with CO_2 in the catalytic cycle (Scheme 27).³¹





 $\label{eq:scheme24} \begin{array}{l} \mbox{Scheme24} & \mbox{Ni-catalyzed regiodivergent carboxylation of allylic alcohol} \\ \mbox{with } \mbox{CO}_2 \end{array}$



 $\mbox{Scheme 25}$ Ni-catalyzed carboxylation of allylic and propargyl alcohols with \mbox{CO}_2

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Scheme 27 The proposed mechanism for the Co-catalyzed carboxylation of propargyl acetates

Carboxylatioin of Alkyl Halides and 7 **Pseudohalides**

In 2014, the Martin group developed the catalytic carboxylation of unactivated primary alkyl bromides 36 with CO₂ with various functional groups (Scheme 28).³² Notably, alkyl sulfonates and trifluoroacetates 38 are also reactive (Scheme 29).³² The reaction is proposed to proceed by a free-radical pathway.

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In 2016, the Martin group developed the catalytic carboxylation of unactivated primary, secondary, and tertiary alkyl chlorides 39 with CO₂ (Scheme 30).³³ The Martin group also described the Ni-catalyzed reductive cyclization/carboxylation of unactivated alkyl halides 40 and 42 with CO₂ under mild conditions. This is an efficient way to synthesize elusive tetrasubstituted olefins **41** ($R^1 \neq H$) (Scheme 31).^{33,34}



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 $\label{eq:Scheme 31} \begin{array}{ll} \mbox{Ni-catalyzed reductive cyclization/carboxylation of unactivated alkyl halides with CO_2 \end{array}$

In 2016, the Martin group employed the nickel-catalyzed reductive carboxylation protocol for the synthesis of cyclopropanecarboxylic acids **44** with carbon dioxide as a C1 synthon (Scheme 32).³⁵ In 2017, the Martin group elegantly developed the nickel-catalyzed chain-walking carboxylation of alkyl halides at remote sp³ C–H sites, which was realized via iterative β -hydride elimination/migratory insertion sequences (Scheme 33).³⁶ The use of ligand **L**₁₁ was crucial in achieving the site-selectivity. This discovery provides an efficient method to convert cheap starting materials into valuable fatty acids.





Scheme 33 Ni-catalyzed carboxylation of discrete alkyl halides at remote sp 3 C–H sites

8 Direct Carboxylation of C-H Bonds

Direct carboxylation of C–H bonds is one of the most straightforward ways to afford carboxylic compounds. The Nolan and Hou groups both independently succeeded in the C–H carboxylation of aromatic compounds using N-heterocyclic carbene (NHC) transition-metal complexes as catalysts. The reaction relies heavily on the acidity of the C–H bonds and uses a gold complex (Scheme 34)³⁷ or a copper complex (Scheme 35).³⁸

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In 2011, the Iwasawa group reported a catalytic nucleophilic carboxylation reaction using carbon dioxide as the carbon source through C–H bond activation (Scheme 36).³⁹ The proposed catalytic cycle is shown in Scheme 37.³⁹ 2-Phenylpyridine undergoes C–H bond activation to form intermediate **F**, which releases methane to afford the key intermediate **G** that reacts with CO₂ via nucleophilic addition.



In 2017, Hou and co-workers developed a copper-catalyzed allylic C–H bond carboxylation of allyl aryl ethers **54** with CO₂, which was achieved through deprotonative alu-



Scheme 37 Proposed catalytic cycle of Rh-catalyzed carboxylation of arylpyridines with CO₂

mination with an aluminum ate compound [*i*-Bu₃Al(TMP)Li] followed by NHC-copper-catalyzed carboxylation of the resulting aryloxy allylaluminum species (Scheme 38).⁴⁰



 $\mbox{Scheme 38}$ Cu-catalyzed carboxylation of allylic C–H bond of allyl aryl ethers with \mbox{CO}_2

Also in 2017, Sato and co-workers developed a catalytic direct allylic $C(sp^3)$ –H carboxylation by using the $Co(acac)_2/Xantphos/AlMe_3$ system, which enabled highly regioselective transformation of allyl groups into linear but-3-enoic acid motifs with good functional group tolerance (Scheme 39).⁴¹ The proposed mechanism suggests a Co¹ intermediate **N** might be crucial in the catalytic cycle and AlMe₃ plays a dual role in the reaction (Scheme 40).⁴¹

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Co(acac)₂ (10 mol%) CO2H Xantphos (20 mol%) 57 AlMe₂ (1.5 equiv) HCI (ag) for 57 CsF, CO₂ (1 atm) 1 pH 4 buffer Ĥ DMA, 60 °C, 12 h 2. CH₂N₂ for 58 56 58 CO_H CO₂H MeC OMe **57a**, 65% 57b. 81% 58a 63% .OEt MaO 57d 63% 58b 41% 57c. 78%

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Scheme 39 Co-catalyzed carboxylation of the allylic C(sp³)–H bond of terminal alkenes with CO₂





Besides these carboxylations of C–H bonds under transition-metal catalysis, some carboxylations of C–H bonds under transition-metal-free⁴² or light-promoted⁴³ conditions were reported, which will not be discussed in detail here.

9 Conclusions and Perspectives

In the past few years, transition-metal-catalyzed carboxylation of electrophiles with carbon dioxide has become a promising new catalytic transformation. However, the development of this field is still in early stages. In particular, site-selective C–H carboxylation is still a challenge. Furthermore, enantioselective carboxylation is another clear frontier in this area. Finally, the development of large-scale catalytic carboxylation reactions with low catalyst loadings is needed.

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