

Carbon Dioxide as a Carbon Source in Organic Transformation: Carbon–Carbon Bond Forming Reactions by Transition-Metal Catalysts

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Recent carbon–carbon bond forming reactions of carbon dioxide with alkenes, alkynes, dienes, aryl zinc compounds, aryl boronic esters, aryl halides, arenes having acidic C–H bonds are reviewed in which transition-metal catalysts play an important role.

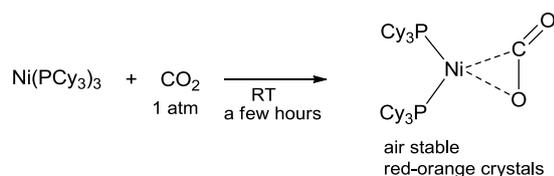
1. Introduction

Carbon dioxide (CO₂) is an ideal carbon source owing to its abundance, low cost, nontoxicity, and good potential as a renewable source.¹ However, it is not easy to activate such a thermodynamically and kinetically stable material. Therefore, catalysts must play an important role to develop useful transformations utilizing this attractive and environmentally friendly raw material. In this review article, recent progress on utilization of CO₂ in carbon–carbon bond forming reactions is surveyed. Such survey will offer basic idea to employ CO₂ as an attractive carbon source in organic transformations. There have been several excellent reviews on a similar subject.² On the other hand, carbon–oxygen bond and carbon–hydrogen bond forming reactions of CO₂ are also important for syntheses of organic carbonates (including CO₂/epoxide copolymerization), formic acid derivatives, and methanol. However, these reactions are not covered in the present article, since several useful reviews are available.^{3d-g, 4e-h}

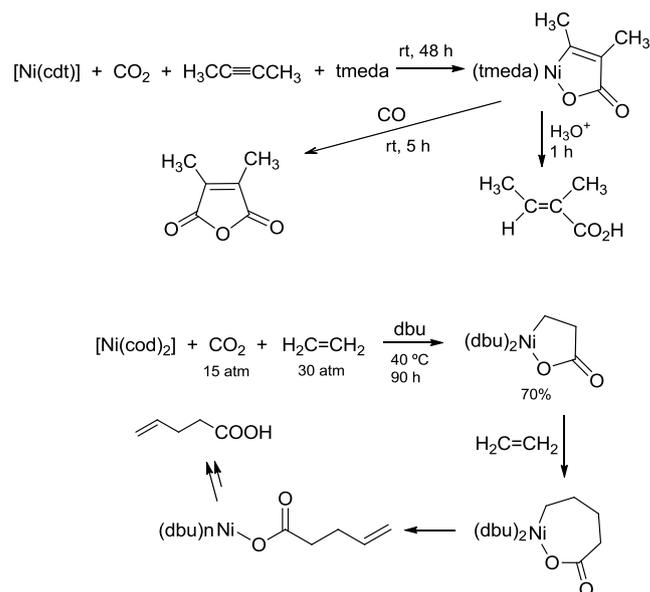
2. Stoichiometric reaction relevant to catalysis with CO₂

2.1 Transition metal complexes bearing CO₂

In order to develop efficient catalytic reactions, fundamental behaviours of CO₂ in the presence of a transition metal complex must be understood. As the first isolated and characterized metal CO₂ complex, Aresta et al. prepared [Ni(CO₂)(PCy₃)₂] (Cy = cyclohexyl) complex in 1975 by treating [Ni(PCy₃)₃] or [{Ni(PCy₃)₂]₂N₂] with CO₂ in toluene. (Scheme 1).⁵ The CO₂ coordinates to the electron rich Ni(0) centre as η² form. This finding suggested that CO₂ could be activated on a metal centre. More relevant to catalytic reactions of CO₂, Hoberg et al. found



Scheme 1 Synthesis of Ni(0) η²-CO₂ complex.

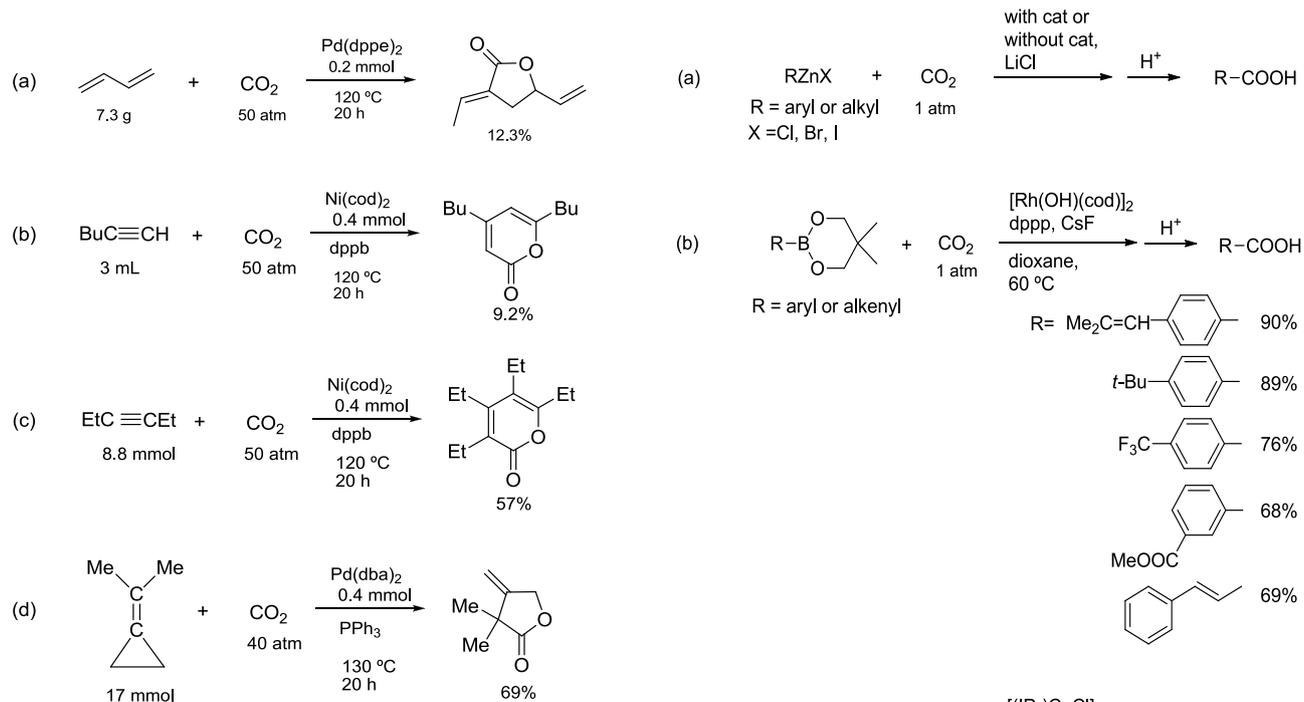


Scheme 2 Stoichiometric reaction of Ni(0) complex in the presence of 2-butyne and ethylene: cdt = 1,5,9-cyclododecatriene, tmeda = *N,N,N',N'*-tetramethylethylenediamine, dbu = 1,8-diazabicyclo[5.4.0]undec-7-ene

that CO₂ reacts with alkenes or alkynes in the presence of a stoichiometric amount of Ni(0) complexes to afford oxanickelacycles (Scheme 2).⁶ Even the metal complexes were used in stoichiometric amounts, useful carbonyl compounds were obtained as products. Furthermore, a wide variety of complexes bearing CO₂ in various coordination styles (η¹, η², μ²-η², μ²-η³, etc.) have been isolated and characterized to date.⁷

2.2 Seminal catalytic reactions of CO₂

A series of pioneering works for catalytic transformation of CO₂ with unsaturated compounds were carried out by Inoue et al. in 1976–1979.^{8a-c} First, they reacted 1,3-dienes under a CO₂ pressure of 50 atm in the presence of a catalytic amount of Pd(dppe)₂ (dppe = Ph₂(CH₂)₂PPh₂) at 120 °C (Scheme 3a).^{8a} They found the lactone formed from CO₂ in a complex mixture of various products. In the presence of Ni(cod)₂–dppe (cod = 1,5-



Scheme 3. Early catalytic reactions of hydrocarbon unsaturates with CO₂. dppe = Ph₂P(CH₂)₂PPh₂, dppb = Ph₂P(CH₂)₄PPh₂, cod = 1,5-cyclooctadiene, dba = dibenzylideneacetone

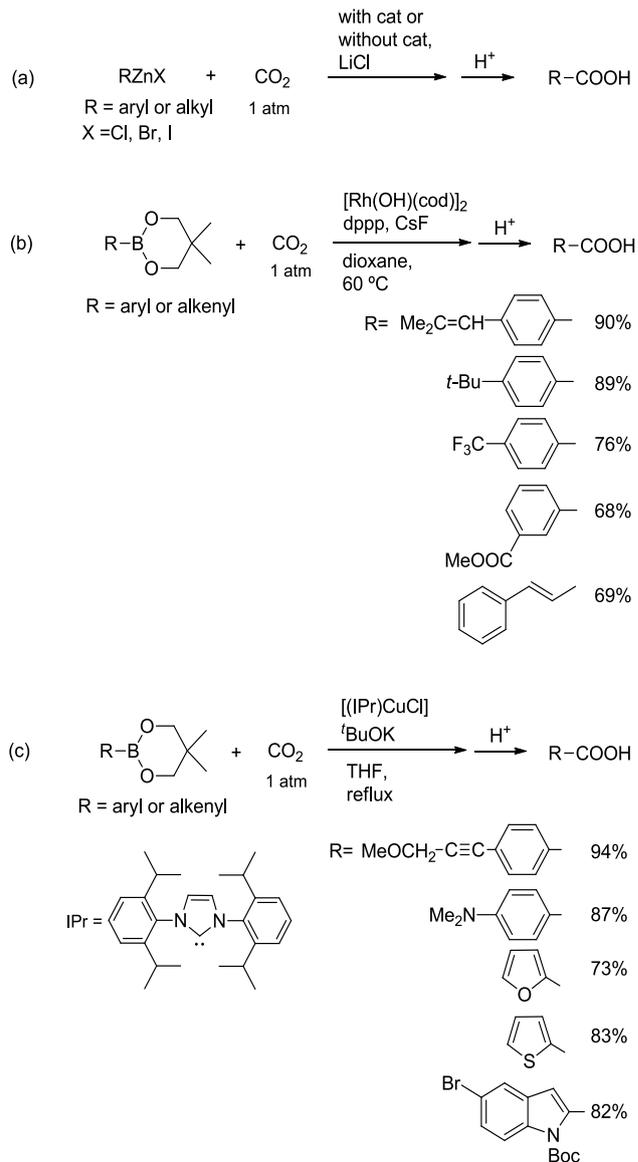
cyclooctadiene, dppb = Ph₂P(CH₂)₄PPh₂) as a catalyst at 120 °C, two terminal alkynes reacted with CO₂ (50 atm) to afford lactones in only low yields (Scheme 3b).^{8b} On the other hands, with the same catalyst system, internal alkynes provided the corresponding products in much higher yields (Scheme 3c).^{8c} As for alkenes, Pd(0) catalyzed reaction of methylenecyclopropanes with CO₂ (40 atm) provided lactones successfully in good yields (Scheme 3d).^{8d} In these reactions, yields of the products from CO₂ were not so satisfactory. However, these results clearly indicated that such catalytic reactions are very useful and promising.

3. Carbon-carbon bond forming reaction with CO₂

Carbon-carbon bond forming reactions are quite important to develop a wide variety of organic transformations employing CO₂. The most classical methods to realize the C-C bond forming reaction with CO₂ are the reaction with Grignard and organolithium reagents. Highly nucleophilic these reagents react with CO₂ without a catalyst. However, in these reactions, many useful functionalities such as ketones, esters, and nitriles are not tolerant. Thus, in order to develop transformations compatible with various functionalities, much less nucleophilic substrates must be employed. In such cases, catalysts are important and indispensable for successful C-C bond formation reactions with CO₂.

3.1 Reactions of Zinc compounds with CO₂

In place of Grignard and lithium reagents, less nucleophilic



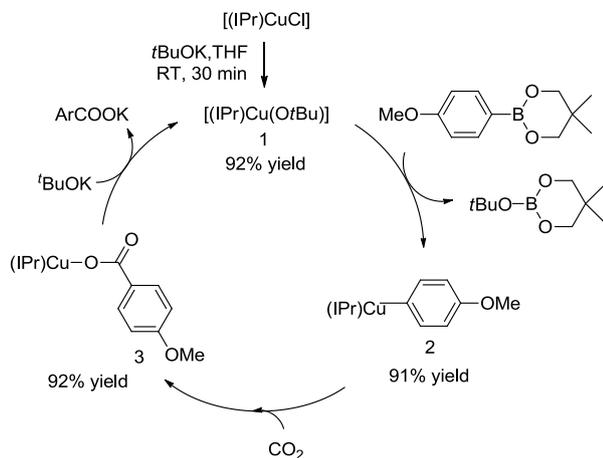
Scheme 4 Carboxylation reactions of organozinc and -borane compounds using CO₂

organozinc were utilized with CO₂ (Scheme 4a), since a wide variety of functionalities are compatible with organozinc compounds. Yorimitsu and Oshima reported that alkylzinc iodide-LiCl readily react with CO₂ in THF in the presence of Ni(acac)₂-PCy₃ as a catalyst to afford the corresponding carboxylic acids.^{9a} They found that the addition of LiCl was essential for the carboxylation. They claimed that the Ni catalyst is indispensable for alkylzinc compounds, while PhZnI-LiCl reacted with CO₂ in THF without the Ni catalyst to afford benzoic acid in 36% yield. Independently, Dong et al reported that carboxylation of arylzinc bromides with CO₂ proceeded in the presence of a similar Ni and Pd catalysts bearing PCy₃ as a ligand.^{9b} They reported that no carboxylation occurred without the transition metal catalyst. On the other hand, Kondo et al found that transition metal catalysts are not necessary for these

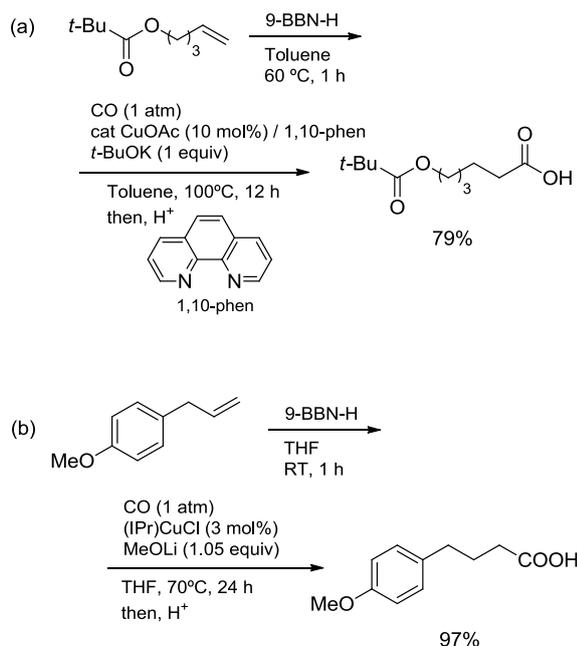
reactions, but only 2.8 equiv of LiCl in DMF is sufficient for the reaction.^{9c} Activities of organozinc compounds seem to be varied considerably depending on reaction conditions, and some reactions really proceed without a transition metal catalyst.

3.2 Reactions of organoboronic esters with CO₂

Organoboron compounds are easily prepared by various methods and are highly useful substrates in a variety of organic synthesis. Iwasawa et al. reported that aryl- and alkenylboronic esters react with CO₂ in the presence of [Rh(OH)(cod)]₂ (3



Scheme 5 Possible catalytic cycles and isolation of catalytic species in Scheme 4c



Scheme 6 Formal reductive carboxylation of terminal alkenes via hydroboration

Table 1 Nickel-mediated 1,4-double-carboxylation of 1,3-diene

1,3-diene	product	yield (%)
		68
		75
		73
		50

10 mol%), dppp (Ph₂P(CH₂)₄PPh₂, 7 mol%), and CsF (3 equiv) to provide the corresponding carboxylic acids in high yields (Scheme 4b).^{10a} In the reaction, ester part of the boronic esters affected the carboxylation considerably. Actually, only 2,2-dimethyl-1,3-propanediolate ester (Scheme 4b) afforded the 1,3-diolate, ethylene glycolate, pinacolate, and catecholate gave almost no products. On the other hand, insertion of CO₂ into carbon-Cu bonds has been known.¹¹ Hou et al. reported that the same carboxylation of organoboronic esters are possible with N-heterocyclic carbene copper catalysts, in which the same effect of the ester moiety was observed (Scheme 4c).^{10b} Importantly, most copper catalytic species (**2** and **3** in Scheme 5) were isolated in high yields (91% and 92%) and fully characterized including X-ray crystal structure analysis. The mechanism shown in Scheme 5 was supported by DFT calculations indicating insertion of CO₂ into the Cu-Ar bond is the rate-determining step in which nucleophilic attack of the aryl moiety on CO₂ affords the new C-C bond.^{10c} Iwasawa et al. reported similar carboxylation by a copper catalyst.^{10d}

30 Sawamura et al. (Scheme 6a)^{12a} and Hou et al. (Scheme 6b)^{12b} independently found that the copper catalyzed carboxylation of alkylboranes were carried out via hydroboration of terminal alkenes with 9-borabicyclo[3.3.1]nonane (9-BBN-H). The overall process represents a useful reductive carboxylation of terminal

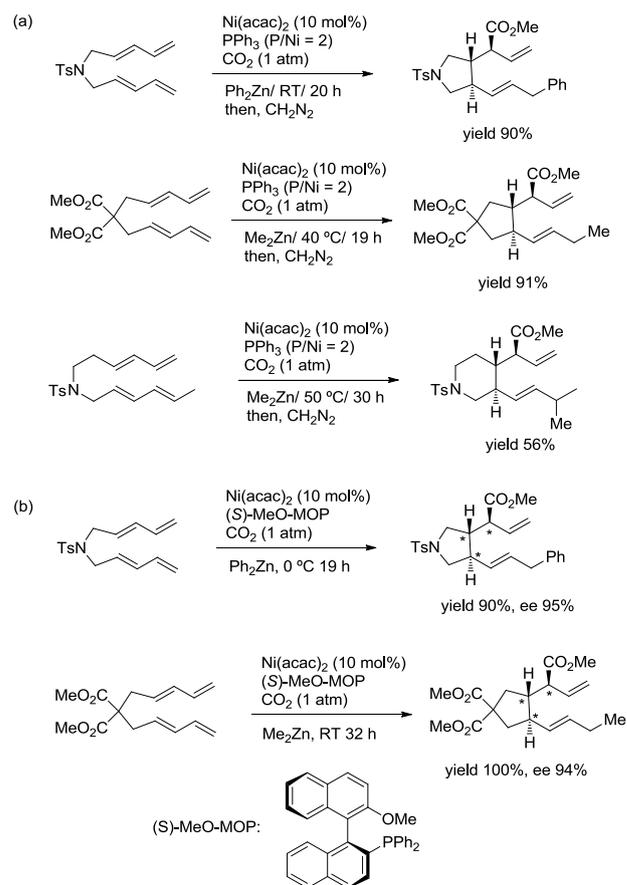
35 alkenes with CO₂.

3.3 Carboxylations of dienes and alkenes

Mori et al. developed carboxylation of 1,3-dienes and allenes with CO₂ via allylnickel intermediates.¹³ When 1,3-dienes were reacted with 1 equiv of Ni(cod)₂ and 2 equiv of dbu under CO₂,

Table 2 Nickel-mediated arylative mono-carboxylation of 1,3-diene

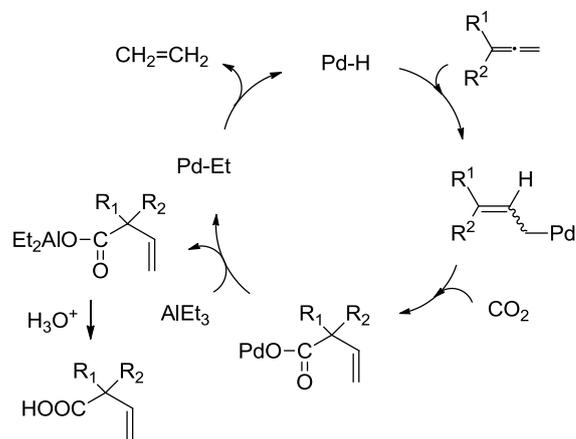
1,3-diene	"ArZn"	product	yield (%)
	Ph ₂ Zn		44
	Ph ₂ Zn		85
		41 : 59	
			48
			77
		43 : 57	



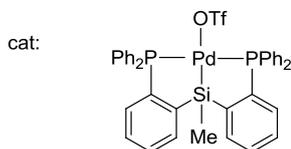
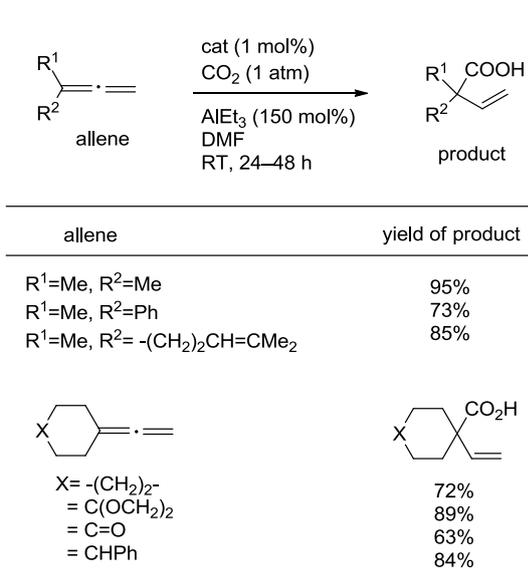
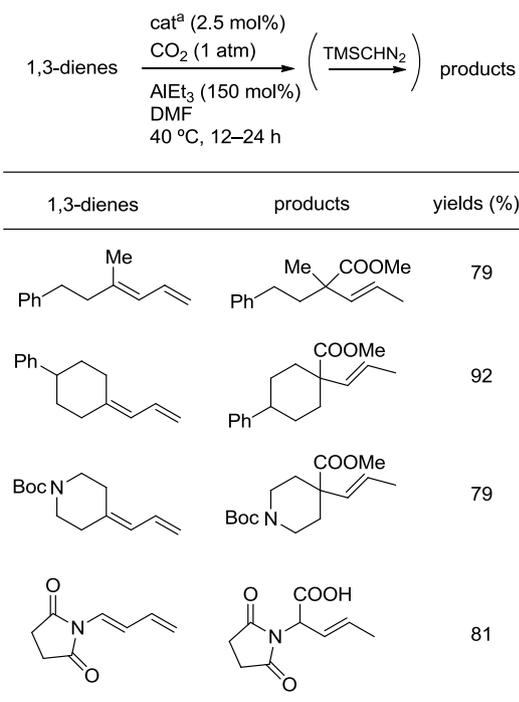
Scheme 7 Nickel-catalyzed ring-closing carboxylation of bis-1,3-dienes

and then further with 5 equiv of Me₂Zn, 1,4-double-carboxylation products were afforded in good yields (Table 1).^{13a} Although the mechanism of the stoichiometric reaction was not clear, the two CO₂ molecules, but no Me moieties, were incorporated in the products. In contrast, when aryl zinc reagents (ArZn) instead of Me₂Zn were employed in the similar stoichiometric reaction, arylative mono-carboxylation proceeded (Table 2).^{13a} Furthermore, by using bis-1,3-dienes as the substrates, the catalytic reaction provided ring-closing carboxylated products regio- and stereoselectively in high yields (Scheme 7a).^{13b} The asymmetric carbonylative cyclization were realized under similar reaction conditions with chiral phosphine ligands (Scheme 7b).^{13c} Mori et al. also found Ni-catalyzed double-carboxylation of trimethylsilyllallene with CO₂^{13d} and Ni-promoted carboxylation/cyclization cascade reaction of allenyl aldehydes.^{13e} In the former case, the silyl moieties were indispensable for the double carboxylation.

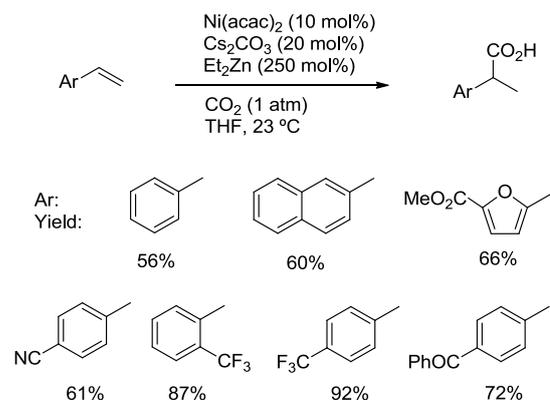
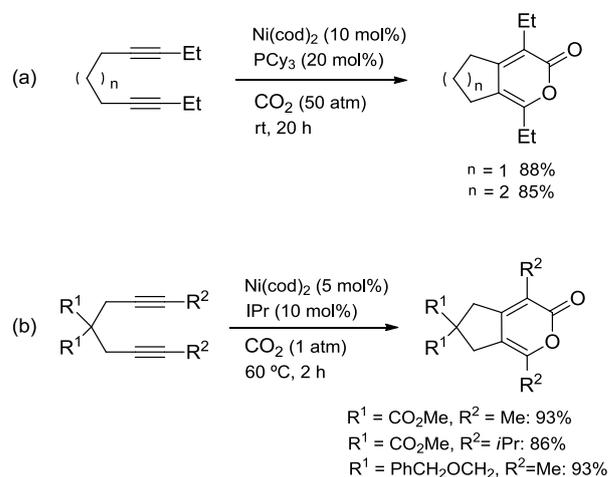
Iwasawa et al. reported hydrocarboxylation of allenes with CO₂ catalyzed by Pd pincer catalyst (Table 3).^{14a} AlEt₃ was employed as a reducing agent and a hydrido source after the β-hydride elimination of the resulting ethyl palladium intermediate (Scheme 8). With a similar Pd catalyst system, one-to-one coupling of 1,3-dienes with CO₂ occurred (Table 4).^{14b}



Scheme 8 Catalytic cycle of Pd-catalyzed hydrocarboxylation of allenes

Table 3 Pd-catalyzed hydrocarboxylation of allenes**Table 4** Pd-catalyzed hydrocarboxylation of 1,3-diene: one-to-one coupling with CO₂

^a The same Pd complex in Table 3 was used as a catalyst

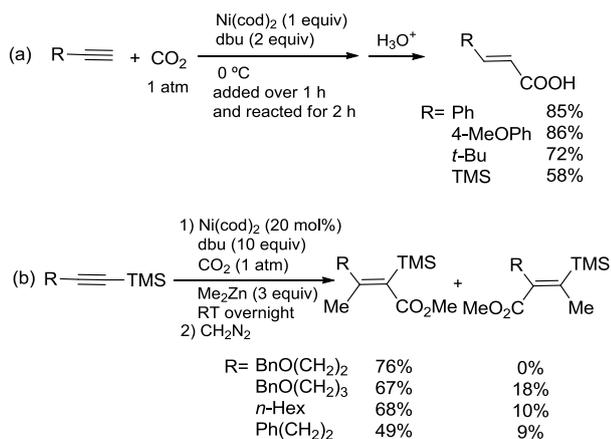
**Scheme 9** Ni-catalyzed reductive carboxylation of styrenes using CO₂**Scheme 10** Carboxylation of α,ω -diynes with CO₂

As for alkenes, Rovis et al. found reductive carboxylation of styrene derivatives with Et₂Zn and CO₂ (Scheme 9).¹⁵ They proposed an insertion on Ni-H into carbon-carbon double bonds of styrenes followed by insertion of CO₂, rather than the Hoberg's metallacycle shown in Scheme 2.

3.4 Carboxylation of alkynes

Pioneering works for catalytic carboxylation of alkynes were carried out by Inoue et al. as shown in Scheme 3b,c.^{8b,c} Tsuda and Saegusa found that the reactions of α,ω -diynes under pressurized CO₂ (50 atm) in the presence of Ni-phosphane catalyst proceeded smoothly and afforded bicyclic α -pyrones in good yields (Scheme 10a).^{16a} In this transformation, IPr ligand in place of phosphanes is much more effective and provided the similar carboxylated products in high yields under 1 atm of CO₂ (Scheme 10b).^{16b}

On the other hand, Yamamoto et al. reported that terminal alkynes reacted with 1 equiv of Ni(cod)₂ and 2 equiv of dbu



Scheme 11 Carboxylation of terminal and TMS acetylenes

under CO₂ (1 atm) at 0 °C in a highly regio- and chemoselective manner (Scheme 11a).^{17a} Similar carboxylation reaction with 1 equiv of Ni(cod)₂ was also carried out using bidentate amidine ligands.^{17b} When alkyl or aryl zinc reagent was added into the Yamaoto's system, alkylative and arylative carboxylation of alkynes proceeded (Table 5).^{17c,e} Interestingly, BuZn reagent afforded the butylated product (entry 3), while Et₂Zn gave hydrocarboxylated product via β-hydride elimination (entry 4). This alkylative carboxylation could be carried out catalytically when trimethylsilyl acetylenes were employed as substrates

Table 5 Carboxylation of alkyne with Ni(cod)₂ and organozinc reagents

entry	"RZn"	equiv	yield (%) ^a	product
1	PhZnCl	2	69	
2	PhCH ₂ ZnCl	1.5	81	
3	BuZnI	3	68	
4	Et ₂ Zn	1.5	9 ^b	

^a Isolated yield based on Ni(cod)₂

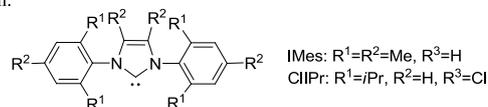
^b in 78% yield

Table 6 Cu-catalyzed hydrocarboxylation of alkyne using CO₂ and hydrosilanes

$R^1-C\equiv C-R^2 \xrightarrow[CO_2 (1\text{ atm})]{Cu\text{ cat}, HSi(OEt)_3 (2\text{ equiv})} R^1-CH=CH-COOH \xrightarrow{H_3O^+}$

alkyne	conditions ^a	product	isolated yield (%)
	A		72
	A		64
	A		52
	A		64
	A		78
	B		74
	C		66

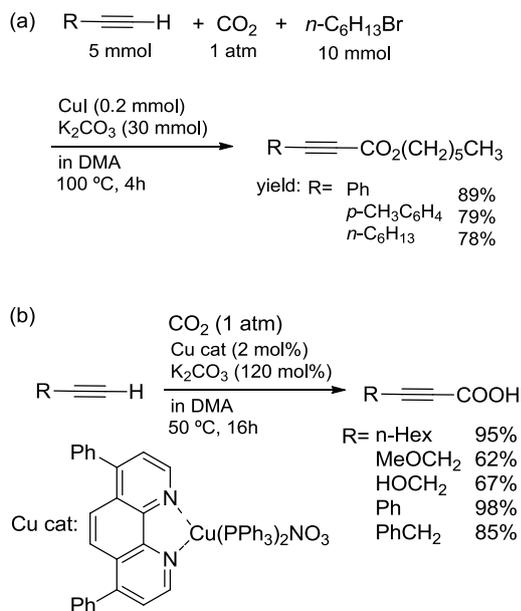
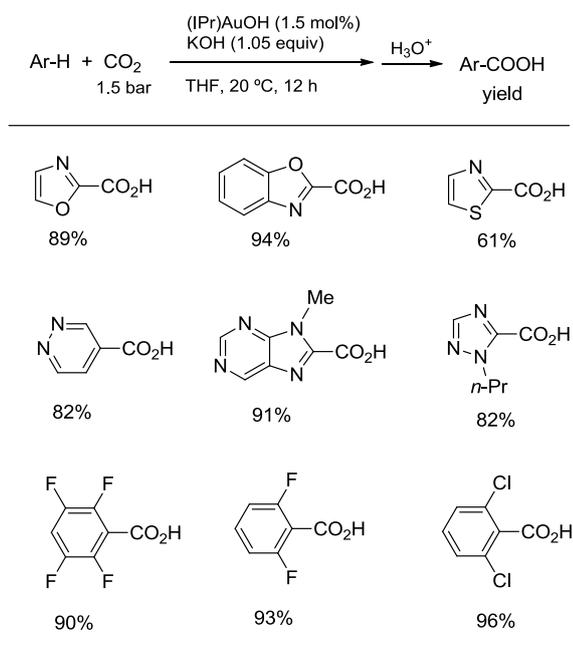
^a Conditions A: IMesCuF (1–2 mol%) in 1,4-dioxane at 100 °C for 12 h. Conditions B: ClIPrCuF (2.5 mol%) in hexane at 70 °C for 14 h. Conditions C: IPrCuF (2.5 mol%) in 1,4-dioxane at 100 °C for 14 h.



(Scheme 11b).^{17d}

In order to utilize CO₂ in C-C bond formations, reducing reagents have been indispensable in the reactions. To date, highly reactive and pyrophoric reagents such as Et₂Zn^{9,15,17a,d,e} and Et₃Al¹⁴ were employed in stoichiometric and catalytic reactions. We recently reported that hydrosilanes, more mild and easy-to-handle reducing reagents, can be used in Cu catalyzed hydrocarboxylation of alkynes.^{18a} Various alkynes were hydrocarboxylated efficiently using HSi(OEt)₃ in good yields (Table 6). In the reactions, HSi(OEt)₃ could be replaced with polymethylhydrosiloxane (PMHS), which is a cheap by-product of the silicon industry. Ma et al. found that the same reaction proceeded with Ni(cod)₂-CsF as a catalyst and Et₂Zn as a reducing reagent.^{18b} Ma also reported methylative carboxylation of homopropargylic alcohols.^{18c}

Inoue et al. found that terminal alkynes reacted with

Table 7 Au-catalyzed carboxylation of aromatic C-H bonds**Scheme 12** Carboxylation of terminal alkynes with CO₂ with and without bromoalkanes

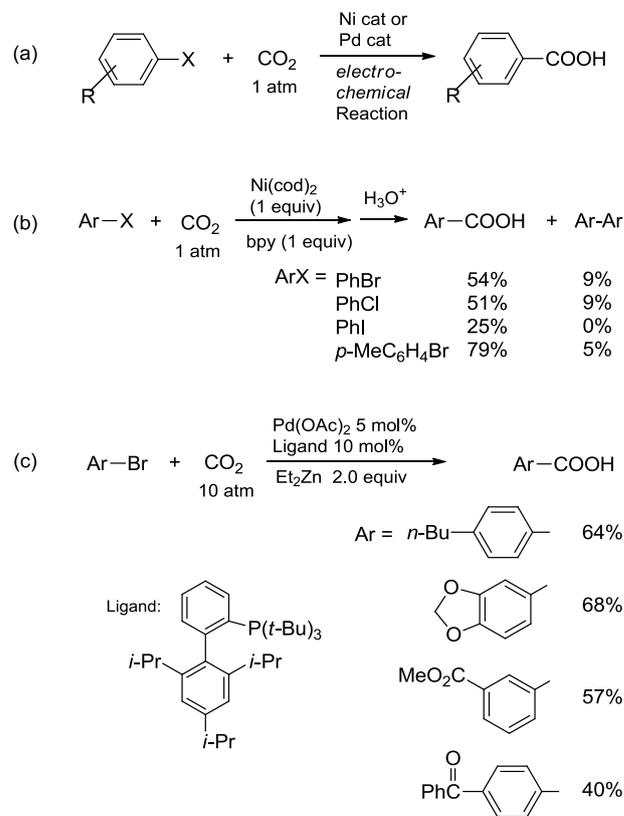
bromoalkanes under CO₂ in the presence of a catalytic amount of CuI.^{19a} Insertion of CO₂ into the acetylenic C-H bonds to give alkyl 2-alkynoates at 100 °C in good yields (Scheme 12a). CuBr, AgI, or AgNO₃ can be utilized as the catalyst successfully. This reaction was applied to one-pot synthesis of arylnaphthalene lactones.^{19b} Recently, IPrCuCl was found to be a more efficient

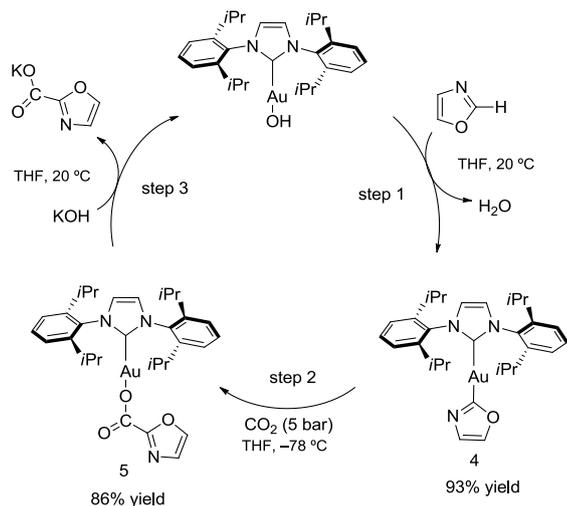
and the reaction proceeded even at lower temperature (60 °C).^{19c} Furthermore, insertion of CO₂ into the C-H bond proceeded without bromoalkanes in the presence of a Cu^{20a,b} (Scheme 12b) or Ag^{20c} catalyst. The same reactions could be carried out without the transition metal catalysts at 120–160 °C, but 2 equiv of Cs₂CO₃ was indispensable.^{20d}

3.5 Carboxylation of aryl halides

As mentioned earlier, the carboxylation reactions of arylzinc (section 2.1) and arylboronic esters (section 2.2) with CO₂ have been studied intensively, since in these reactions various functionalities that are compatible unlike with Grignard reagents. However, these zinc and boron compounds must be prepared from the corresponding aryl halides prior to the catalytic reactions. Thus, the direct carboxylation of the parent aryl halides is most desirable as this is a more straightforward transformation.

The catalytic carboxylation of aryl halides employing CO₂ was first developed as *electrochemical* reactions in the presence of nickel^{21a-c} and palladium catalysts (Scheme 13a).^{21d,e} Unfortunately, these were not efficient synthetic methods, and the scope of possible substrates was quite restricted. Later, the non-electrochemical carboxylation of aryl bromides and chlorides using CO₂ was carried out in the presence of *stoichiometric* amounts of Ni(0) complexes and 2,2'-bipyridine (bpy) (Scheme 13b).^{22a} Recently, the carboxylation of aryl bromides employing CO₂ was performed *catalytically* using a palladium complex as the catalyst.^{22b}

**Scheme 13** Carboxylation of aryl halides with CO₂



Scheme 14 Stoichiometric reactions relevant to the catalytic cycle

3.6 Carboxylation of arenes having acidic C-H bonds

The Kolbe-Schmitt salicylic acid synthesis from sodium phenolate and CO_2 is an early example of carboxylation of C-H bonds. Such direct carboxylation of C-H bonds must be more sustainable transformations. Recently, Nolan et al. reported that $(\text{IPr})\text{AuOH}$ can perform the activation of C-H bonds of electron-deficient arenes.^{23a} They found that the same Au(I) complex is very active for carboxylation of aromatic acidic C-H bonds ($\text{p}K_a$ values < 30) with CO_2 (Table 7).^{23b} The possible catalytic cycle for the present C-H carboxylation (Scheme 14) is similar to the mechanism postulated for Cu(I) catalyzed carboxylation of organoboron esters (Scheme 5). The authors confirmed the mechanism by stoichiometric reactions (Scheme 14). Protonolysis of $(\text{IPr})\text{AuOH}$ by 1 equiv of oxazole gave the intermediate **4**, which was isolated in 93% yield (step 1). Reaction of **4** by saturating the solution with CO_2 at -100°C afforded carboxylate complex **5** in 86% isolated yield (step 2). Finally, $(\text{IPr})\text{AuOH}$ was regenerated upon metathesis of **5** with 1 equiv of KOH with precipitation of potassium oxazole-2-carboxylate (step 3). Hou et al.^{23c} and Nolan and coworkers^{23d} independently reported that Cu catalysts are active as catalysts in the carboxylation reaction of the acidic C-H bonds (Table 8).^{23c} Hou isolated catalytic intermediates (arylcopper and copper carboxylate) in a stoichiometric reaction and determined the structures by X-ray crystallographic analysis.^{23c} However, these C-H carboxylations could proceed with only a base (Cs_2CO_3 is most suitable) at 125°C .^{23c} Iwasawa et al. found the first C-H carboxylation with CO_2 via chelation-assisted C-H activation. Various 2-arylpiperidines and 1-arylpiperazoles afforded carboxylated products in the presence of a Rh catalyst and a stoichiometric amount of $\text{AlMe}_2(\text{OMe})$ (Table 9).

Table 8 Cu-catalyzed carboxylation of aromatic C-H bonds

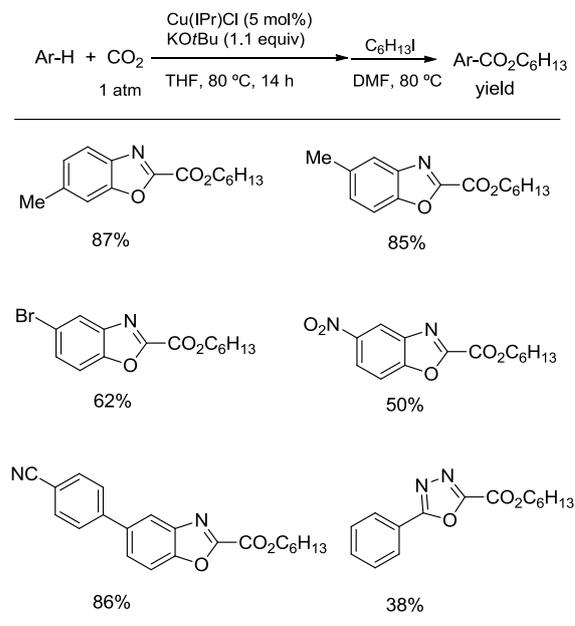
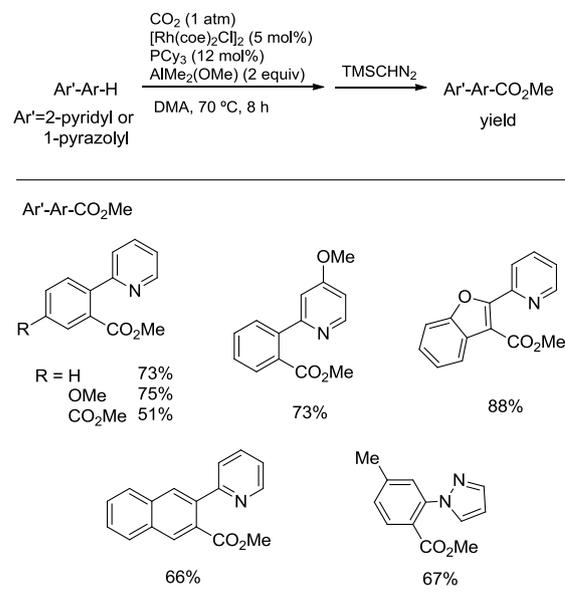


Table 9 Rh-catalyzed direct carboxylation of arenes via chelation-assisted C-H bond activation



35 Conclusions

Carbon dioxide (CO_2) can be utilized in carbon-carbon bond forming reactions with the aid of transition-metal catalysts. Organozinc compounds usually do not react with CO_2 without a transition-metal catalyst, and Ni and Pd catalysts are active to

afford the corresponding carboxylic acids. Organoboron esters are also useful substrates which are reacted with CO₂ to provide the carboxylic acids in the presence of Rh and Cu catalysts. In the Cu-catalyzed reaction, aryl-Cu or ArCOOCu intermediates were isolated and fully characterized. Dienes, alkenes, and alkynes were efficiently reacted with CO₂ in the presence of Ni, Pd, and Cu catalysts. Usually, highly reactive and pyrophoric reducing reagents such as Et₂Zn and Et₃Al are indispensable in the reactions. Recently, easy-to-handle hydrosilanes such as HSi(OEt)₃ and polymethylhydrosiloxane (PMHS) can be employed with a Cu catalyst. Carboxylation of aryl halides and arenes having acidic C–H bonds are realized.

Notes and references

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