1. Introduction

Much attention has been paid to use of carbon dioxide (CO2) as a readily available carbon source1)2). However, CO2 is not easy to activate because of its thermodynamic and kinetic stability. Therefore, transition-metal catalysts will be important role in developing useful transformations by utilizing this available and environment-friendly raw material.

Three important methodologies are available to achieve the transition metal-catalyzed fixation of CO2 (Scheme 1). The carbon-hydrogen bond-forming reactions of CO2 are important for the syntheses of C1 chemicals such as formic acid derivatives, methanol, and methane (Scheme 1a)3)6). CO2 is known to react with suitable reducing agents such as molecular hydrogen, hydrosilanes, and hydroboranes. Organic carbonates can be synthesized by the carbon-oxygen bond-forming reactions of CO2 with epoxides (Scheme 1b)7)12). The resultant polycarbonates are important industrial materials. The carbon-carbon (C-C) bond-forming reactions of CO2 are straightforward methods for synthesizing diverse carboxylic acids and their derivatives (Scheme 1c)12)20). The reactions of CO2 with Grignard and organolithium reagents are the classical C-C bond-forming reactions with CO2. The high nucleophilicity of these reagents allow the reaction with CO2 in the absence of a catalyst, but many useful functional groups such as ketones, esters, and nitriles cannot be present during these reactions.

Catalytic fixation of CO2 via C-C bond formation has been extensively investigated during the last decade. The most important factor in catalytic fixation of CO2 is formation of the M-C bond, where M is the transition metal used as the catalyst. Three main steps have been reported for the catalytic fixation of CO2 (Scheme 2). The first step is a substitution-type reaction (Scheme 2a). The M-C bond can be formed catalytically by the oxidative addition of organic halides (C-X) or transmetalation with organometallic reagents. Then, insertion of CO2 into the M-C bond forms the corresponding carboxylic acids. In oxidative addition, catalytic carboxylation of organic halides can be achieved using a suitable reducing agent21)28). The carboxylation reactions of aryl and alkylzinc reagents29)31) as well as aryl22)24)34), allyl35), and alkylboron36)37) compounds with CO2 have been widely studied, because...
various functional groups that are not compatible with Grignard reagents are compatible with these reactions. The second step is addition of the catalytically generated organometallic species to C–C multiple bonds (Scheme 2b). In particular, the hydrocarboxylation reaction is very promising, including addition of M–H species across C–C multiple bonds such as alkynes, alkynes, 1,2-dienes (allenes), and 1,3-dienes, followed by trapping CO₂. The third step is oxidative cyclization of a low-valent transition metal such as Ni(0) with C–C unsaturated compounds (alkene or alkyne), and CO₂, resulting in the corresponding metallacycle intermediate (Scheme 2c). Interesting catalytic transformations have often been reported using these elemental steps.

The present review describes the Ni- and Cu-catalyzed fixation of CO₂ which was established in our laboratory. The most important factor for the four successful transformations is the catalytic formation of M–C bonds (M = Ni or Cu) and regeneration of catalytically active species using suitable reagents. The possible substrates and mechanisms of these reactions are discussed.

2. Nickel Catalysts

2.1. Carboxylation of Aryl Chlorides

Carboxylation of organic halides is one of the most straightforward methods to synthesize various carboxylic acids. The first catalytic carboxylation of aryl bromides using CO₂ and highly reactive ZnEt₂ as the reducing agent was reported in 2009. To achieve high yields of the products, the reaction was carried out under a CO₂ pressure of 10 atm (1 atm = 1.01325 × 10⁵ Pa) at 40 °C. We reported a much more efficient catalytic reaction, in which a less noble metal Ni catalyst was highly active in the carboxylation of aryl chlorides under 1 atm pressure of CO₂ at room temperature using easy-to-handle Mn powder as the reducing agent. The reaction of 1-buty1-4-chlorobenzene (1a) was carried out using a mixture of NiCl₂(PPh₃)₂ (5.0 mol%) and PPh₃ (10 mol%) as the catalyst and Mn powder (3.0 equiv.) as the reducing agent in the presence of tetraethylammonium iodide (Et₄NI, 10 mol%) in 1,3-dimethyl-2-imidazolidinone (DMI) at 25 °C under 1 atm pressure of CO₂. After derivatization to the corresponding methyl ester with trimethylsilyldiazomethane, methyl 4-buty1benzoate (2a-Me) was obtained in 95 % GC yield. In the absence of NiCl₂(PPh₃)₂, Mn powder or Et₄NI, the carboxylation reaction did not proceed at all, indicating that every component is essential for the reaction. Under the optimum reaction conditions, 4-buty1benzoic acid (2a) was isolated in 84 % yield.
organolithium or organomagnesium reagents, were well tolerated under these reaction conditions (2f-2 h). A boronic acid ester (2i) and a thiophene ring (2j) also remained intact.

To elucidate the catalytic mechanism, stoichiometric reactions were carried out using NiPhCl(PPh3)2 (3), which was prepared by the oxidative addition of chlorobenzene to Ni(PPh3)4 (Scheme 5). In the presence of CO2 (1 atm pressure), Mn powder, Et4NI, and Ph3P, afforded the carboxylated product (2k-Me) in 47% yield after derivatization to the corresponding methyl ester. However, removal of either Mn powder or Et4NI from the reaction systems resulted in only a trace amount of 2k-Me. Thus, both Mn and Et4NI are indispensable in the catalytic system and may reduce the Ni(II) to the corresponding Ni(I). The Ni(I) species must be important in the present catalytic carboxylation reaction.

Scheme 6 shows a possible catalytic cycle for the Ni-catalyzed carboxylation of aryl chlorides (1).

(a) Ni-mediated reaction of 1,3-butadiene, and (b) Ni-catalyzed reaction of silyl-substituted allenes.

Using a similar protocol, we established the Co-catalyzed carboxylation of propargyl acetates (4) (Scheme 7). Using Mn under 1 atm pressure of CO2 in the presence of a Co catalyst, various propargyl acetates were converted to the corresponding carboxylic acids (5) in good to high yields.

2.2. Double Carboxylation of Alkynes

Double carboxylation reactions, in which two CO2 molecules are introduced simultaneously into a C-C unsaturated molecule, are highly promising for the efficient synthesis of dicarboxylic acid derivatives. An elegant stoichiometric double carboxylation of 1,3-butadienes in the presence of a Ni(0) complex (Scheme 8a) has been described56). 1-(Trimethylsilyl)-3-allyl-substituted allenes were used as the substrate in the first catalytic double carboxylation with a Ni catalyst (Scheme 8b)57).

Recently, we reported Ni-catalyzed double carboxylation of internal alkynes with CO2, resulting in highly versatile maleic anhydrides as the products (Scheme 9)58). The reaction of 5-decyne (6a) was investigated using Ni(acac)2(bpy) (10 mol%, acac = acetylacetonate; bpy = bipyridine) as the catalyst, Zn powder (3.0 equiv.) as the reducing reagent, and MgBr2 (2.0 equiv.) as the additive in the presence of molecular sieves 3 Å (1 Å = 10-10 m, MS 3 Å, powder) in N,N-

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dimethylformamide (DMF) at room temperature under 1 atm pressure of CO₂. Under these conditions, the double-carboxylated product 7a was obtained in 74 % GC yield. However, the reaction failed using Ni(acac)₂ as the catalyst (i.e., without the bpy ligand). MgBr₂ and Zn powder were essential for the reaction. Without MS 3 Å, the yield of product 7a decreased slightly.

Under the optimal reaction conditions, 7a was obtained in 71 % isolated yield (Scheme 10). Using 3-hexyne (6b) and 2,9-dimethyl-5-decyne (6c) as the substrates, products (7b and 7c) were obtained in good isolated yields. 2-Octyne (6d) and 5-phenyl-2-pentyne (6e) reacted smoothly, resulting in the corresponding products. A cyclic internal alkyne (6f) also reacted, giving the product (7f) in 79 % yield. An alkyne with a C = C bond (6g) was converted to the corresponding product (7g). Alkynes with secondary alkyl groups on the sp-carbons (6h and 6i) also formed the double-carboxylated products (7h and 7i) in good yields. Unfortunately, terminal alkynes and aromatic internal alkynes did not result in the corresponding double-carboxylated products.

This reaction was applied to the rapid and highly efficient synthesis of Chaetomellic acid A anhydride, which is isolated from the coelomycete Chaetomella acutiseta(57). The reaction of commercially available 1-hexadecyne with methyl iodide formed the corresponding internal alkyne 6j in 96 % yield (Scheme 11). The treatment of 6j under optimized reaction conditions resulted in the desired product (7j) in 70 % isolated yield. This is the shortest and most efficient reported synthetic route to Chaetomellic acid A anhydride.

To elucidate the reaction mechanism of the unique double carboxylation reaction, stoichiometric reactions as well as DFT calculations were carried out. As described above, oxidative cyclization of Ni(0), CO₂, and alkynes forms the corresponding oxanickelacyclopentenones. In fact, the reaction of 5-decyne (6a) with Ni(COD)₂ (CO = 1,5-cyclooctadiene) in the presence of bpy under CO₂ (1 atm) gave the corresponding complex 8a in 75 % isolated yield (Scheme 12a). The double carboxylation of 6a proceeded in the presence of a catalytic amount (10 mol%) of the complex 8a resulting in 63 % yield (Scheme 12b), indicating the involvement of nickelacycle 8 in the catalytic cycle.

Regarding incorporation of the second CO₂, the DFT calculations indicate that an intermediate (8b) was formed first as an adduct with MgBr₂, followed by one-electron reduction of intermediate 8b with Zn in the presence of MgBr₂, forming a Ni(I) intermediate (Scheme 13). After one-electron reduction of intermediate 8b to B, the insertion of CO₂ into the Ni-C bond of B1 became very favorable (∆G°⁺ = 5.0 kcal/mol). In the one-electron reduction, MgBr₂ is essen-
tial for providing bromide ion to Zn(II). During the CO₂ insertion, the resulting MgBr coordinates with both the carboxylate moiety and incoming CO₂ in B₁ and TS₁₂₃ to facilitate the second carboxylation. Thus, the presence of MgBr₂ allows the one-electron reduction of intermediate 8b and accelerates the CO₂ insertion in B₁.

Based on the experimental results and the DFT calculations, a plausible catalytic cycle is suggested (Scheme 14). The active catalyst species may be the Ni(0) complex with a bpy ligand (A) which is formed by reduction of the Ni(II) catalyst precursor with Zn (step a). Then, the oxidative cyclization of Ni(0) complex A with alkyne 6 and CO₂ forms a Ni(II) metallacycle 8 (step b). The reduction of 8 with Zn and MgBr₂ gives Ni(I) species B (step c). B must be a key intermediate in this double carboxylation, because the carboxylation of B to C (step d) is much easier due to the higher nucleophilicity of B and coordinative participation of the MgBr moiety. Finally, the reduction of C results in the double-carboxylated product D and regenerates the active Ni(0) catalyst species (step e).

3. Copper Catalysts

3.1. Hydrocarboxylation of Alkynes

Copper hydride (CuH) is an efficient reducing agent in organic synthesis. Various CuH catalyzed reductions of carbonyl compounds such as ketones and aldehydes have been reported employing hydrosilane, which is an easy-to-handle and stable reducing agent. In addition, the CuH species adds across nonpolar C-C bonds, generating reactive organocopper intermediates.

We observed that Cu complexes catalyzed the hydrocarboxylation of alkynes using CO₂ and hydrosilane as the reducing agent. The reaction of diphenylacetylene (9a) with CO₂ (balloon) was carried out using HSi(OEt)₃ as the reducing agent in dioxane at 100 ºC (Scheme 15). The yield of (E)-2,3-diphenyl-2-propenoic acid (10a) was determined by GC after derivatization to the corresponding methyl ester (10a-Me).

Using IMesCuF as the catalyst, 10a-Me was obtained in 86 % yield. Using IPrCuF as the catalyst, which is a bulkier catalyst compared to IMesCuF, the yield of 10a-Me decreased to 41 %. When HSi(OEt)₃ was replaced with polymethylhydrosiloxane (PMHS) that is an inexpensive, easy-to-handle, and environmentally-friendly reducing agent, 10a-Me was obtained in 80 % yield. Toluene was an effective solvent, affording 10a-Me in 81 % yield.

The hydrocarboxylation of diverse symmetrical aromatic alkynes (9b-9h) was carried out in the presence of IMesCuF as the catalyst (Scheme 16). From all the alkynes listed, the corresponding α,β-unsaturated carboxylic acids (10b-10h) were obtained in good isolated yields with perfect (E) stereochemistry. The reaction of alkynes bearing both electron-rich and electron-deficient aryl moieties afforded the corresponding products in good yields. Importantly, bromo (10d), alkoxy carbonyl (10e) and cyano (10f) functional groups were tolerated in the reaction. As for terminal alkynes, phenylacetylene (9i) was converted to cinnamic acid (10i) in 44 % yield when IPrCuF was used as the catalyst.
In the hydrocarboxylation of 1-phenyl-3,3-dimethyl-1-butyne (9j), using Cl$_2$IPrCuF (2.5 mol%) in hexane as the solvent at 70 °C, a single isomer (10j) was obtained in 71% yield (Scheme 17). Reaction of an alkyne with a cyclohexyl group (9k) afforded the corresponding product (10k) in high yield. In the case of 1-phenyl-1-hexyne as the substrate, a mixture of regioisomers (10l) was obtained in high yield and with good selectivity. Moreover, the reaction of 1,4-dimethoxy-2-butyne (9m) and 2,5-dimethoxy-3-hexyne (9n) bearing two propargylic ether functional groups also formed the corresponding products (10m and 10n) in good yields.

To investigate the reaction mechanism, stoichiometric reactions were carried out (Scheme 18). Treatment of Cl$_2$IPrCuF with excess (4 equiv.) hydrosilane such as PMHS or HSi(OEt)$_3$ in C$_6$D$_6$ caused an immediate color change from colorless to bright orange. The $^1$H NMR spectrum of the product indicated the formation of pure Cl$_2$IPrCuH with the peak of Cu-H at 2.39 ppm, which was comparable to that for IPrCuH (2.67 ppm). Reaction of an aromatic alkyne for 2.5 h at room temperature smoothly formed the corresponding alkenyl-copper complex. Reaction with CO$_2$ (balloon) was very slow at room temperature, but proceeded at a higher reaction temperature (65 °C) for 12 h, giving a carboxylato-copper complex. Finally, treatment with excess (4 equiv.) HSi(OEt)$_3$ at room temperature smoothly afforded Cl$_2$IPrCuH.

Based on the stoichiometric reactions, a catalytic cycle is proposed as shown in Scheme 19. A CuH species (A) is generated in-situ from LCuF (L = IMes, IPr, or Cl$_2$IPr) and hydrosilane because of strong Si–F interactions (step a). The syn addition of A to an alkyne (10) initiates the catalytic cycle and stereoselectively...
forms a copper alkenyl intermediate (B) (step b). Then, insertion of CO2 gives the corresponding carboxylato copper intermediate (C) (step c). Finally, σ-bond metathesis of C with hydrosilane provides the corresponding silyl ester and regenerates A (step d).

3.2. Silacarboxylation of Alkynes

Catalytic heterocarboxylation, in which the heteroatom and CO2 are simultaneously and catalytically incorporated into unsaturated substrates, is extremely useful, because the reaction using CO2 provides a valuable synthetic route for highly functionalized carboxylic acid derivatives. Previously, boracarboxylation of alkynes was achieved using Cu catalysts and bis(pinacolato)diboron as the boron source.

We reported the first catalytic silacarboxylation of internal alkynes employing CO2 and silylborane in the presence of a Cu catalyst (Scheme 20). The reaction of 1-phenyl-1-propyne (11a) was carried out using readily available Me2PhSi-B(pin) as the silicon source in the presence of a Cu catalyst in octane at 100 °C under CO2 at 1 atm pressure. A mixture of CuCl and PCy3 (P/Cu = 1) was used as the catalyst, forming silalactones in 97 % yield with high regioselectivity. PBu3 also acted as an efficient ligand, and the products were obtained regioselectively in high yield. However, PPh3 and PPh3 were not efficient ligands. Reaction using IMesCuCl gave 12a in high yield, but with slightly lower regioselectivity. [CuCl(PCy3)]2 prepared from CuCl and PCy3 was the best catalyst, forming silalactone 12a in quantitative yield while maintaining high regioselectivity. Using toluene and 1,4-dioxane as the solvent, the products were obtained in 98 % and 84 % yields, respectively, whereas reaction using acetonitrile and DMF failed.

The reactions of 1-aryl-1-propynes bearing both electron-rich and electron-deficient substituents on the aryl ring formed the corresponding silalactones (Scheme 21). Fortunately, the bromo (12d) and ester (12e) functional groups remained intact under these reaction conditions. Reactions of 1-phenyl-1-hexyne (11f) and a conjugated enyne (11g) resulted in the corresponding products (12f and 12g) in 70 % and 76 % yields, respectively. Diphenylacetylene (11h) also formed the corresponding product (12h) in good isolated yield with a longer reaction time, whereas the reaction of 5-decyne (11i) at 90 °C for 2 h afforded 12i in 81 % yield.

Control experiments were carried out (Scheme 22) to elucidate the silacarboxylation mechanism. The reaction may proceed stepwise via two sequential known reactions, i.e., silaboration of the alkyne followed by carboxylation of the resulting vinylboronic ester.

Based on these observations, a possible catalytic cycle for the silacarboxylation of alkynes with CO2 is proposed (Scheme 23). First, reaction of the alkoxo-
copper species with silylborane forms the silylcopper complex (A)\(^6\). The syn addition of A to an alkyne 11 initiates the catalytic cycle and forms the \(\beta\)-silylalkenylcopper intermediate B (step a). Then, the insertion of CO\(_2\) into the Cu-C(vinyl) bond gives the corresponding Cu carboxylato species (C) (step b). The intramolecular cyclization via C forms the phenylcopper species D, providing the silalactone (12) (step c). Finally, the \(\sigma\)-bond metathesis of D with silylborane gives PhB(pin), and the silylcopper species (A) is regenerated (step d).

The phenyl moiety on the Si is crucial for efficient Si-C bond cleavage because reaction with Et\(_3\)Si-B(pin) instead of Me\(_2\)PhSi-B(pin) resulted in the corresponding silalactone in a trace amount. Moreover, GC and GC-MS analysis of the reaction mixture showed that PhB(pin) was formed in the reaction.

### 4. Summary

We demonstrated that CO\(_2\) can be utilized in C-C bond-forming reactions. Ni complexes catalyzed the carboxylation of less reactive aryl chlorides and double carboxylation reactions of alkynes in the presence of Mn or Zn powder as the reducing agent. Hydrocarboxylation of alkynes was achieved using Cu catalysts and hydrosilanes. Cu-catalyzed silacarboxylation of alkynes was established by using silylborane as the silylation reagent. Using these reactions, diverse products such as benzoic acids, maleic anhydride derivatives, acrylic acid derivatives, and silalactones were synthesized in good to high yields from CO\(_2\). These results indicate that it is important to select the optimum combination of transition-metal catalysts and suitable reducing agents for catalytic CO\(_2\) fixation. Hopefully, these methodologies will contribute to the synthesis of many valuable molecules from CO\(_2\).

![Scheme 23 Plausible Reaction Mechanism of Copper-catalyzed Silacarboxylation of Alkynes (11)](image)

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要旨

遷移金属錯体触媒を用いた炭素-炭素結合形成を経る二酸化炭素固定化反応

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二酸化炭素を炭素資源として利用する研究が近年、注目を集めている。しかしながら、その熱力学的安定性のため化学反応に用いられるのは様々な制限があった。本報では、均一系遷移金属錯体触媒を用いた炭素-炭素結合形成反応を経る二酸化炭素固定化反応について、我々が見出した四つの反応を紹介する。ニッケル触媒を用いた例として、塩化アリル類のカルボキシル化反応およびアルキルのダブルカルボキシル化反応を取り上げる。これらの反応は、取り扱いの容易なマンガナラジに亜鉛粉末を還元剤として用いて適温な条件で進行する。鋼触媒を用いた例として、ヒドロシラノンを用いたアルキンのヒドロカルボキシル化反応およびシリンリンを用いたアルキンのシラカルボキシル化反応を紹介する。シラカルボキシル化反応では、ケイ素原子を含む環状ラクトンであるシララクトンが得られる。いずれの反応においても、反応条件の最適化、基質適用範囲ならびに反応機構の詳細について述べる。