[Review Paper]

Transition-metal Catalyzed Synthesis of Carbonyl Compounds Using Formates or Formamides as Carbonyl Sources

Tetsuaki FUJIHARA and Yasushi TSUJI *

Dept. of Energy and Hydrocarbon Chemistry, Graduate School of Engineering, Kyoto University, Nishikyo-ku, Kyoto 615-8510, JAPAN

(Received August 24, 2017)

Various available approaches for catalytic carbonylation reactions using formates and formamides with transition metal catalysts are reviewed. Pd complexes catalyze the hydroesterification or hydrocarbonylation of alkynes using aryl formates or formamides, respectively, as the carbonyl sources. The esterification of aryl halides with aryl formates proceeds in the presence of a Pd catalyst with suitable ligands. Using a Cu complex with a bulky bidentate phosphine ligand is used as a catalyst, boraformylation and silaformylation of allenes efficiently proceeds using alkyl formates as a formyl source.

Keywords
Formate, Formamide, Homogeneous catalysis, Palladium, Copper

1. Introduction

Carbon monoxide (CO) is an important C1 unit which is often used as a carbonyl source to convert various bulk chemicals into functionalized products in large-scale application for industrial syntheses. However, carbonylation reactions with CO are not typically used in the laboratory-scale synthesis of complex organic molecules, probably due to general reluctance to use a toxic gas as a reagent, as well as the required use of high-pressure reactors. Therefore, carbonylation reactions without the use of external CO are highly desirable.

Formic acid and its esters can be industrially produced from CO. These compounds are stable and easy-to-handle in laboratory-scale syntheses. Consequently, formate esters are expediently alternative sources of CO for laboratory-scale syntheses. In this context, considerable efforts have been made to develop carbonylation reaction employing formate esters or related carbonyl compounds as a CO sources. Skrydstrup and co-workers established Pd-catalyzed ex-situ generation of CO. They also reported the generation of CO from silylcarboxylic acids or CO2 in the presence of suitable activators. Manabe and co-workers reported the generation of CO from formates or formylsaccaline and their applications in Pd-catalyzed carbonylation reactions.

This review describes Pd-catalyzed hydroesterification and hydrocarbonylation of alkynes employing formates or formamides as the carbonyl sources, respectively. Esterification of aryl halides with aryl formates also proceeds in the presence of a Pd catalyst. Cu-catalyzed bora- and silaformylation of allenes employing an alkyl formate is also possible. The scope of substrates and plausible reaction mechanisms are discussed.

2. A Use of Formates

2.1. Transformation with Formates: Overview

Hydroesterification of carbon–carbon (C–C) multiple bonds is an important and atom-economic synthetic method for elongating carbon chains, giving a wide variety of esters.

In 1983, Sneed and co-workers reported the Ru-catalyzed hydroesterification of ethylene with methyl formate. Kondo and Mitsudo found that a Ru complex catalyzed the hydroesterification of norbornene and ethylene. In 2002, Chang and co-workers reported the Ru-catalyzed hydroesterification of alkynes with chelating formates under mild reaction conditions. Manabe and co-workers also found the Ru-catalyzed hydroesterification of alkynes with formates, in which the use of a hydroxymethyl imidazole ligand was effective and a mixture of the corresponding esters was obtained.

DOI: doi.org/10.1627/jpi.61.1
* To whom correspondence should be addressed.
* E-mail: ytsuji@scl.kyoto-u.ac.jp
Regarding the esterification of aryl halides, Manabe and co-workers reported the Pd-catalyzed esterification with phenyl formate (Scheme 2(a))\textsuperscript{12,13}. Using formylsaccharine and hydrosilanes as the formyl and hydride sources, respectively, the formylation of aryl halides smoothly proceeded in the presence of a Pd catalyst (Scheme 2(b))\textsuperscript{15}).

### 2.2. Pd-catalyzed Hydroesterification of Internal Alkynes

In 2011, we found that a Pd complex catalyzed the hydroesterification of alkynes with aryl formates\textsuperscript{22}). Reaction of phenyl formate (1a) and diphenylacetylene (2a) was carried out in the presence of a catalytic amount of Pd(OAc)_2 (Scheme 3). Addition of monodentate phosphines such as PPh\textsubscript{3}, P(o-tol)_\textsubscript{3}, and PCy\textsubscript{3} afforded the hydroesterificated product (3a) in low yields. The use of bidentate phosphines such as dppe and dpbb improved the catalytic activity. Xantphos gave the best result, affording 3a in 99 % yield with perfect (E)-stereoselectivity. Unfortunately, alkyl formates such as butyl formate (1b) and benzyl formate (1c) were not converted at all, but phenyl formate (1a) was a good substrate in this hydroesterification reaction.

During the course of the catalytic reaction, facile conversion of aryl formates into the corresponding phenols and CO was observed. Therefore, the hydroesterification proceeded via the formation of carbon monoxide and phenols from aryl formates. Zero order dependence on the concentration of aryl formates was observed with up to 80 % conversion. Furthermore, the nature of ligands strongly affected the rate constant of the conversion of 1a (Scheme 4). Without phosphine ligands, no conversion of 1a was observed. Bidentate phosphate ligands such as xantphos and dppe showed high efficiency, but dppe was not a suitable ligand (Scheme 3) and xantphos exhibited a high efficiency in the hydroesterification reaction.

Various internal alkynes were converted to the corresponding phenols and CO was observed. Therefore, the hydroesterification proceeded via the formation of carbon monoxide and phenols from aryl formates. Zero order dependence on the concentration of aryl formates was observed with up to 80 % conversion. Furthermore, the nature of ligands strongly affected the rate constant of the conversion of 1a (Scheme 4). Without phosphine ligands, no conversion of 1a was observed. Bidentate phosphate ligands such as xantphos and dppe showed high efficiency, but dppe was not a suitable ligand (Scheme 3) and xantphos exhibited a high efficiency in the hydroesterification reaction.

Various internal alkynes were converted to the corresponding products under the optimized reaction conditions (Scheme 5). Di(4-methylphenyl)acetylene and di(4-acetylphenyl)acetylene afforded the corresponding
products 3b and 3c in high yields. 5-Decyne was also converted into the corresponding product in a high yield. Among unsymmetrical alkynes, 1-phenyl-1-propyne provided two regioisomers, but the major product (3e) was isolated in pure form in 64 % yield. 1-Phenyl-2-(trimethylsilyl)ethyne afforded 3f selectively as a single regioisomer in 96 % yield. 1-Cyclohexyl-1-propyne gave a mixture of regioisomers and the major isomer (3g) was isolated in 79 % yield. Aryl formates bearing both electron-rich (1d) and electron-poor (1e and 1f) phenyl moieties gave the corresponding products (3h-3j) in high yields. Terminal alkynes were also successfully utilized in the hydroesterification reaction using a mixture of Pd2(dba)3 and xantphos as the catalyst (Scheme 6). The reaction of phenylacetylene with 1a proceeded regioselectively, giving 3k as a single regioisomer in 93 % yield. 4-Ethynyltoluene and 1-ethynyl-4-methoxybenzene also regioselectively afforded the corresponding products, 3l and 3m. Other terminal alkynes with alkyl or silyl substituents on the sp carbon also afforded the corresponding products in high yields with high regioselectivities.

A plausible catalytic cycle is shown in Scheme 7. Aryl formate 1 is converted into the corresponding phenol and CO in the formate conversion cycle (left cycle in Scheme 7). As described above, kinetic measurements indicated that the rate has zero order dependence on the concentration of 1. Therefore, precoordination of 1 to active catalyst species A with a large equilibrium constant might be involved. The formate conversion cycle must be faster than the hydroesterification cycle, since phenols and carbon monoxide accumulated in the reaction system. The generated phenols might react with catalyst species A to afford C. Insertion of the alkynyl forms alkenyl intermediate D (step 1), and insertion of CO affords intermediates E or E' (step 2). Finally, reductive elimination results in the hydroesterification product (3) and the active catalyst species (A) is regenerated (step 3).

2.2. Pd-catalyzed Esterification of Aryl Halides

We developed the Pd-catalyzed esterification of aryl halides employing aryl formates as the CO source23). By simply mixing aryl halides, an aryl formate, and a Pd catalyst in a glass flask, the highly efficient esterification of aryl halides was achieved. The same reaction system was independently reported by Manabe and co-workers as described above (Scheme 2a)12).

Reaction of 4-bromotoluene (4a) with 1.5 equiv. of phenyl formate (1a) was carried out in the presence of a catalytic amount of PdCl2(PhCN)2 (Scheme 8). Without a ligand, phenyl 4-methylbenzoate (5a) was not obtained. Addition of monodentate phosphines such as PPh3, P(o-tol)3, or PCy3, gave 5a in low yields. Use of bidentate phosphines such as dppe, dppp, or dppf improved the catalytic activity. Xantphos gave the best result, affording 5a in 99 % yield. As for
base, (i-Pr)2EtN, DBU, and K2CO3 afforded 3a in 82, 70, and 57% yields, respectively. Under the reaction conditions with xantphos as the ligand, alkyl formates such as benzyl formate (1c) and hexyl formate (1g) were not converted, and the corresponding esters were not obtained.

Conversion of 1a was monitored under various reaction conditions (Scheme 9). In the presence of a catalytic amount (2.5 mol%) of PdCl2(PhCN)2 and xantphos with 1.0 equiv. of Et3N, phenol was obtained quantitatively together with the evolution of CO. Removal of Et3N resulted in low conversion of 1a and low yield of phenol. In contrast, with only 1.0 equiv. of Et3N, 1a was fully converted and the phenol was obtained in 99% yield. Thus, Et3N was responsible for the conversion of 1a. In the presence of Et3N, alkyl formates such as 1c and hexyl formate (1g) were not converted, as with the catalytic reaction.

Various aryl bromides were reacted with 1a under the optimized reaction conditions (Scheme 10). Aryl bromides bearing both electron-donating and electron-withdrawing substituents gave the corresponding esters (5b-5h) in high yields. Heterocycles such as pyridine and thiophene were also viable (5i and 5j). Reaction of bromobenzene with aryl formates bearing electron-rich and electron-poor phenyl moieties gave the corresponding esters (5k and 5l) in good to excellent yields. In particular, a sterically crowded aryl formate also afforded the desired product (5m).

An alkenyl bromide (6) reacted with 1a under the standard reaction conditions to give phenyl cinnamate (5n) in 66% yield (Scheme 11(a)). Iodobenzene (7) and phenyl triflate (8) were converted into phenyl benzoate (5o) in 85% and 88% yields, respectively (Scheme 11(b)). Although a chloro moiety on the aryl ring remained intact under the standard reaction conditions (5d in Scheme 10), an aryl chloride bearing an acetyl moiety (9) gave the corresponding ester (5e) in 86% yield at higher temperature using (i-Pr)2EtN as the base (Scheme 11(c)). In addition, benzyl bromide (10) was smoothly converted into the corresponding phenyl ester (5p) by using P(OMe)3, as a ligand at 120°C (Scheme 11(d)).

A plausible catalytic cycle is shown in Scheme 12. Aryl formate (1) is converted into the corresponding phenol and CO in the presence of a base. Oxidative addition of aryl bromides with Pd(0) initiates the catal-
lytic cycle and generates the arylpalladium intermediate \( B \). Then, CO reacts with \( B \) to afford acylpalladium species \( C \). Ligand exchange between \( Br \) and \( OAr \) generates the intermediate \( D \). Finally, reductive elimination results in the desired ester \( 5 \) and the active catalyst species \( A \) regenerates.

2.4. Cu-catalyzed Boraformylation and Silaformylation of Allenes

Formates were used as a formyl source in Claisen-type condensation reactions\(^{24,25}\). We found that boraformylation of allenes could be achieved by employing \( B_2\text{(pin)}_2 \) and a formate ester as the boron and formyl sources, respectively, in the presence of a copper catalyst\(^{26}\).

Reaction of 3-methyl-1,2-nonadiene (11a), \( B_2\text{(pin)}_2 \), and hexyl formate (1g) was carried out at 50 °C by employing 3.0 mol% of \( \text{CuOAc} \) and 4.0 mol% of a ligand in toluene (Scheme 13). As for ligands, \( \text{PPh}_3 \), dppe, xantphos, dppbz, and \( \text{Xy-dppbz} \) were ineffective in the catalytic reaction. DTB-dppbz and DTBM-dppbz ligands selectively afforded the product 12a in 99% and 96% yields, respectively.

Using DTBM-dppbz as the ligand, various allenenes were employed as substrates under optimized reaction conditions (Scheme 14). 1,1-Dialkyl-substituted allenes were converted into the corresponding \( \beta \)-boryl-\( \beta,\gamma \)-unsaturated aldehydes (12a-12c) in good to excellent isolated yields. Allenes bearing several functionalities such as terminal olefins, \( C(\text{sp}^2) \)-halogen bonds, ester and carbamate groups provided the corresponding products (12d-12h) in moderate to good isolated yields in the presence of sodium laurate (20 mol%).

When the reaction of 11a with \( \text{PhMe}_2\text{Si-B(pin)} \) and 1g was conducted in THF at 60 °C, silaformylation product 13 was obtained in 88% yield (Scheme 15). Various allenenes gave the corresponding \( \beta \)-silyl-\( \beta,\gamma \)-unsaturated aldehydes in good to excellent yields. Functionalities such as terminal olefin, \( C(\text{sp}^3) \)-halogen bonds, acetal and ester were tolerated. The corresponding silaformylation product (13i) was obtained from the mono-substituted allene in a moderate yield.

J. Jpn. Petrol. Inst., Vol. 61, No. 1, 2018
Both bora- and silaformylation proceeded via similar catalytic cycles (Scheme 16). First, boryl copper species \( \text{A} \) is generated by the reaction of \( \text{B}_2(\text{pin})_2 \) with \( \text{Cu} \) compounds\(^{27} \). A silyl copper species is also afforded upon reaction of \( \text{PhMe}_2\text{Si-B}(\text{pin}) \) with copper compounds\(^{28} \). Then, \( \text{A} \) adds across the terminal double bond of allene \( 11 \), generating \( \beta \)-boryl and \( \beta \)-silyl allyl-copper intermediates (step 1). Next, \( \text{B} \) reacts with a formate ester at the \( \gamma \)-position to provide \( \text{C} \) via a six-membered ring transition state (step 2). \( \beta \)-Elimination from \( \text{C} \) produces \( 12 \) \( (Y = \text{B}(\text{pin})) \) and \( 13 \) \( (Y = \text{SiMe}_2\text{Ph}) \) by extruding the alkoxycopper species \( \text{D} \) (step 3). Finally, \( \sigma \)-bond metathesis of \( \text{D} \) with \( \text{B}_2(\text{pin})_2 \) and \( \text{PhMe}_2\text{Si-B}(\text{pin}) \) regenerates the active catalyst species (step 4).

### 3. A Use of Formamides

#### 3.1. Transformation with Formamides: Overview

Addition of formamides to unsaturated C-C bonds substrates is an efficient atom-economic synthetic method to provide a variety of amides. In 1999, Kondo and Mitsudo reported the Ru-catalyzed addition of formamides to norbornene and ethylene\(^{18} \). These reactions did not require carbon monoxide even under the harsh reaction conditions (Scheme 17(a)). In 2003, Chang and co-workers reported the Ru-catalyzed addition of formamides with chelating formamides (Scheme 17(b))\(^{29} \). As for alkynes, Takemoto and co-workers reported an intramolecular reaction with a Rh catalyst (Scheme 17(c))\(^{30} \). In 2009, intermolecular addition to alkynes was first reported by Nakao, Hiyama and co-workers in the presence of a Ni(0) catalyst combined with strong Lewis acids such as \( \text{AlMe}_3 \) (Scheme 17(d))\(^{31} \). Notably, the reaction proceeded under very mild conditions (35-80°C). They also applied the Ni/Lewis acid system to the hydrocarbamoylation of alkenes\(^{32} \). Nozaki and Hiyama reported the Pd-catalyzed aminocarbonylation of aryl bromides with DMF in the presence of POCl\(_3\) (Scheme 17(e))\(^{33} \). Later, Lee and co-workers found that a Ni complex with a phosphite ligand catalyzed the aminocarbonylation of aryl bromides and iodides\(^{34} \).

#### 3.2. Ruthenium-catalyzed Hydrocarbamoylation of Alkenes

In 1987, our group reported the first example of the addition of formamides to alkenes in the presence of Ru\(_3\)(CO)\(_{12}\) under a CO atmosphere (Scheme 18)\(^{35} \). Reaction of \( N\)-(n-octyl)formamide (14a) and 1-hexene (15a) was carried out in the presence of a catalytic amount of Ru\(_3\)(CO)\(_{12}\). A mixture of the linear and branched adducts (16a) was obtained in a good yield with moderate selectivity under a high CO pressure (20 kg cm\(^{-2}\)) at 200°C. CO pressure and temperature strongly affected the efficiency of the reaction.

The reactions of cyclic alkenes such as cyclohexene and cyclopentene with formamides afforded the corresponding products in high yields (Scheme 19).

A plausible catalytic cycle is shown in Scheme 20. Oxidative addition of the C-H bond of formamide with
Ru(0) initiates the reaction and the corresponding Ru-H intermediate B is formed (step 1). Addition of Ru-H to the alkene affords alkylruthenium intermediate C (step 1). Finally, reductive elimination of C provides the desired product and regenerates the Ru(0) species A (step 3).

3.3. Pd-catalyzed Hydrocarbamoylation of Alkynes

We also reported the Pd-catalyzed addition of formamides to alkynes\(^3\). The reaction of N,N-dimethylformamide (DMF, 14d) with diphenylacetylene (2a) in the presence of a catalytic amount (2.5 mol\%) of PdCl\(_2\)(PhCN)\(_2\) and xanthos was performed (Scheme 21). When anhydrous HCl (50 mol\%) was added to the catalyst system, the desired product 17a was obtained in 82\% yield. The reaction of HCl with Pd compounds provides a Pd-H species\(^3\).

In a Pd catalyzed reaction, acid chlorides were useful additives to generate Pd-H species in-situ\(^3\). Actually, hexanoyl chloride as an additive (20 mol\%) afforded the product in 99\% yield. Benzoyl chloride also gave the product in a high yield. In this case, HCl was most likely generated by the reaction of benzoyl chloride with DMF with concomitant formation of CO (detected by GC). The addition of Brønsted acids such as trifluoroacetic acid only afforded a trace amount of the product. Without any additives, the desired product was not obtained.

Various formamides and internal alkynes were viable substrates in the reaction and gave the corresponding products in good to high yields (Scheme 22). Di(4-acetylphenyl)acetylene with 14d afforded the corresponding product (17b) stereoselectively in 72\% yield. An alkyne bearing thiophene rings smoothly afforded the corresponding product (17c) in 90\% yield. 5-Decyne also provided the corresponding product (17d) with high stereoselectivity and in a high yield. As for unsymmetrical alkynes, even the reaction with a simple hydrocarbon alkyne proceeded with good regioselectivity. Alkynes bearing ester moieties could be employed in the reaction. Other formamide derivatives were converted into the corresponding adducts in good to high yields.

Various terminal alkynes also afforded the products in high yields with excess 14d using the same Pd catalyst system (Scheme 23). Reaction of phenylacetylene with 14d gave the adducts in 96\% yield as a mixture of regioisomers 17k and 17k’ in an 89/11 ratio. Products (17l and 17l’) were obtained from 2-ethynyltoluene in high yields with high regioselectivity. Aliphatic terminal alkynes also afforded the corresponding products as mixtures of two regioisomers (17m).
carbonyl sources affords the hydroesterification or generated by the oxidative addition of the formyl C-H product and regenerates. Finally, hydrocarbamoylation products in the presence of Pd catalysts. Aryl formates can be converted into the corresponding aryl esters via the Pd-catalyzed esterification of aryl halides. Alkyl formates such as hexyl formate serve as a formyl source in the Cu-catalyzed boraformylation and silaformylation of allenes. Hopefully, these methodologies will contribute to efficient syntheses of many valuable molecules.

References

1) Kollár, K., “Modern Carbonylation Methods,” Wiley-VCH, Weinheim (2008).
2) Beller, M., “Catalytic Carbonylation Reactions,” Springer, Heidelberg (2006).
3) Colquhoun, H. M., Thompson, D. J., Twigg, M. V., “Carbonylation: Direct Synthesis of Carbonyl Compounds,” Plenum, New York (1991).
4) Morimoto, T., Kakiuchi, K., Angew. Chem. Int. Ed., 43, 5580 (2004).
5) Konishi, H., Manabe, K., Synlett, 25, 1971 (2014).
6) Wu, L., Liu, Q., Jackstell, R., Beller, M., Angew. Chem. Int. Ed., 53, 6310 (2014).
7) Gautam, P., Bhanage, B. M., Catal. Sci. Technol., 5, 4663 (2015).
8) Friis, S. D., Lindhardt, A. T., Skrydstrup, T., Acc. Chem. Res., 49, 594 (2016).
9) P. Hermange, P., Lindhardt, A. T., Taaning, R., K. Bjerglund, K., Lupp, D., Skrydstrup, T., J. Am. Chem. Soc., 133, 6061 (2011).
10) Friis, S., Taaning, R., Lindhardt, A. T., Skrydstrup, T., J. Am. Chem. Soc., 133, 18114 (2011).
11) Lian, Z., Dennis, U., Nielsen, Lindhardt, A. T., Daasbjerg, K., Skrydstrup, T., Nat. Commun., 7, 13782 (2016).
12) Ueda, T., Konishi, H., Manabe, K., Org. Lett., 14, 3100 (2012).
13) Ueda, T., Konishi, H., Manabe, K., Org. Lett., 14, 5370 (2012).
14) Konishi, H., Ueda, T., Manabe, K., Org. Synth., 91, 39 (2014).
15) Ueda, T., Konishi, H., Manabe, K., Angew. Chem. Int. Ed., 52, 8611 (2013).
16) Konishi, H., Fukuda, M., Ueda, T., Manabe, K., Org. Synth., 94, 66 (2017).
17) Isnard, P., Denise, B., Sneeden, R. P. A., Cognion, J. M., Durupal, P., J. Organometallic. Chem., 256, 135 (1983).
18) Kondo, T., Okada, T., Mitsudo, T., Organometallics, 18, 4123 (1999).
19) Ko, S., Na, Y., Chang, S., J. Am. Chem. Soc., 124, 750 (2002).
20) Konishi, H., Ueda, T., Muto, T., Manabe, K., Org. Lett., 14, 4722 (2012).
21) Ren, W., Chang, W., Wang, Y., Li, J., Shi, Y., Org. Lett., 17, 3544 (2015).
22) Katafuchi, Y., Fujihara, T., Iwai, T., Terao, J., Tsuji, Y., Adv. Synth. Catal., 353, 475 (2011).
23) Fujihara, T., Hosoki, T., Katafuchi, Y., Iwai, T., Terao, J., Tsuji, Y., Chem. Commun., 48, 8012 (2012).
24) Mariella, R. P., J. Am. Chem. Soc., 69, 2670 (1947).
25) Frank, R. L., Varland, R. H., Org. Synth., Coll. Vol. 3, 829 (1955).
26) Fujihara, T., Sawada, A., Yamaguchi, T., Tani, Y., Terao, J., Tsuji, Y., Angew. Chem. Int. Ed., 56, 1539 (2017).
27) Laitar, D. S., Müller, P., Sadighi, J. P., J. Am. Chem. Soc., 127, 17196 (2005).
28) Klebeberg, C., Cheung, M. S., Lin, Z., Marder, T. B., J. Am. Chem. Soc., 133, 19060 (2011).
29) Ko, S., Han, H., Chang, S., Org. Lett., 5, 2687 (2003).
30) Kobayashi, Y., Kaminiski, H., Yanada, K., Yanada, R., Takemoto, Y., Tetrahedron Lett., 46, 7549 (2005).
31) Nakao, Y., Idei, H., Kanyiya, K. S., Hiyama, T., J. Am. Chem.

Scheme 23 Scope of Substrates in Pd-catalyzed Hydrocarbamoylation of Terminal Alkynes (2) with 14d

and 170’) in good yields with good regioselectivity. In these reactions, major regioisomers were easily and efficiently isolated in analytically pure form by column chromatography.

A plausible catalytic cycle was shown in Scheme 24. Pd-H species A is the key catalytic intermediate. Hydropalladation of an alkyne initiates the catalytic cycle form alkynylpalladium intermediate B (step 1). Insertion of the C=O bond of formamide results in the corresponding alkoxypalladium intermediate C (step 2). Finally, β-hydride elimination of G provides the desired product and regenerates A (step 3). Alternatively, a mechanism involving Pd(IV) intermediate D that is generated by the oxidative addition of the formyl C-H bond of a formamide might be possible. In this case, reductive elimination from D could provide the desired product, and regenerates A.

4. Summary

Formate esters and formamides are useful reagents for transition-metal-catalyzed carbonylation reactions. Reactions of alkynes using formates or formamides as carbonyl sources affords the hydroesterification or hydrocarbamoylation products in the presence of Pd catalysts.

J. Jpn. Petrol. Inst., Vol. 61, No. 1, 2018
要旨

遷移金属錯体触媒を活用するジ酸エステルまたはホルムアミドを原料としたカルボニル化合物の合成反応

藤原 哲晶, 辻 康之
京都大学大学院工学研究科物質エネルギー化学専攻, 615-8510 京都市西京区京都大学桂

カルボニル化合物は自然界に広く存在する重要な化合物群である。これら化合物の迅速かつ高効率な合成手法の開発は、複雑な分子の合成が求められる近年の有機合成反応開発において極めて重要な課題である。遷移金属錯体触媒を用いる合成反応はカルボニル化合物を得るための強力な手法の一つであり、一酸化炭素をカルボニル源とする反応は古くから活用されてきた。しかしながら、一酸化炭素は有毒なガスであり取扱いが困難であることや、一酸化炭素の金属への過剰配位による触媒失活がしばしば問題となる。近年では、一酸化炭素を用いないカルボニル化合物の合成法開発が注目を集めている。本報告では、均一系遷移金属錯体触媒を活用し、ジ酸エステルまたはホルムアミドを原料とするカルボニル化合物の合成反応について述べる。我々が開発したパラジウム触媒を用いた例として、ジ酸エステルおよびホルムアミドを用いたアルキンのヒドロエステル化反応およびヒドロアルカロモル化反応を取り上げる。これらの反応は、原子効率の高い付加反応の形式で反応が進行する。また、ジ酸エステルを用いたパラジウム触媒による反応に伴う環化アリール類のエステル化反応についても紹介する。触媒を用いた例として、ジ酸エステルをカルボニル源とした1,2-ジエン（アレン）のポラノールカルボニル化反応およびシラノールカルボニル化反応を取り上げる。いずれの反応においても、反応選択性、基質適用範囲ならびに反応機構について述べる。