Oxidative Carbonylation

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Oxidative Carbonylation Reactions: Organometallic Compounds (R−M) or Hydrocarbons (R−H) as Nucleophiles

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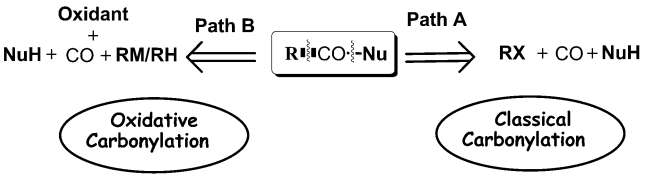
carbonylation · hydrocarbons · nucleophiles · organometallic chemistry · oxidation

Oxidative carbonylation reactions have attracted broad interest from both academia and industry in recent years. Enormous efforts have gone into the syntheses of carbonate and urea derivatives through the oxidative carbonylation of alcohols and amines. Very recently, organometallic reagents (R−M) and hydrocarbons(R−H) were directly employed as nucleophiles to construct a C−C bond in oxidative carbonylation reactions. This Minireview summarizes this novel type of oxidative carbonylation reaction.

1. Introduction

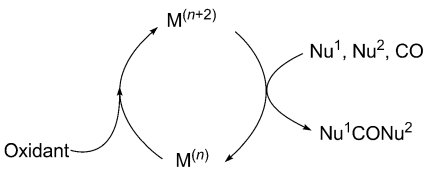
Transition-metal-catalyzed carbonylation of organic halides (RX) with CO, pioneered by Heck and co-workers,[1,2] has attracted much interest in the past 40 years with wide applications in both the laboratory and industry.[3–8] Being a fundamental and promising transformation, the carbonylation process introduces a new approach for constructing a synthetically versatile carbonyl group with high efficiency and selectivity. However, CO as a π acceptor renders low-valent metal catalysts such as Pd^0 species relatively electron deficient, thus increasing the difficulty of oxidative addition of organohalides towards Pd^0 species.[9] Consequently, as shown in the Scheme 1, Path A usually requires harsh conditions such as high temperatures and high CO pressures.[10,11] In addition, the starting materials, R−X, which act as the electrophiles are normally prepared from the corresponding nucleophiles (R−H) including arenes, alkynes, alkenes, and alkanes. Obviously, it would be more straightforward if R−H could be used directly in carbonylation reactions. As shown in Scheme 1, Path B is the oxidative carbonylation process leading to carbonylated derivatives from two nuclephiles with the assistance of an oxidant; this approach has drawn considerable attention in recent years.[12,13]



Scheme 1. Comparison of the classical carbonylation (Path A) and the oxidative carbonylation (Path B).

Scheme 2 shows that two nucleophiles in the presence of CO could react with the transition-metal catalyst $M^{(n+2)}$, which could in turn generate the carbonylation product Nu^1CONu^2 and the metal catalyst in a reduced state ($M^{(n)}$). The oxidant could oxidize $M^{(n)}$ into $M^{(n+2)}$ to promote the catalytic cycle.

Oxidative carbonylation reaction might proceed under milder conditions as it avoids the difficult oxidative addition of metal catalyst with electrophile ArX, which is usually inhibited by the high concentration of CO in classical carbonylation reactions. Moreover, the substrates of oxidative carbonylation reactions are all nucleophiles, many of which are more widely available. If R−H could be directly employed as the nucleophile, it would greatly reduce the cost of the carbonylation process. The oxidants applied in oxidative carbonylation reactions are usually organic compounds or inorganic salts, such as benzoquinone (BQ), $CuCl_2$, silver salts, etc. In some cases, oxygen or air can be efficient oxidants in oxidative carbonylation process. Thus, the oxidative



Scheme 2. General reaction scheme for the oxidative carbonylation.

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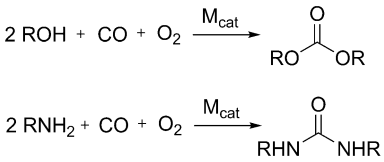
carbonylation reaction could be potentially a more environmentally benign and efficient process to produce many versatile carbonyl derivatives.

One of the most important types of oxidative carbonylation reactions is the synthesis of carbonates and ureas. Organic carbonate and urea compounds play a significant role as pharmaceutical candidates, agrochemicals, resin precursors, dyes, green solvents, and fine additives to petrochemicals and polymers.[14–26] Traditional synthetic methods of these compounds rely heavily on the use of toxic and corrosive reagents, such as phosgene or isocyanates. Easy-handling and less-wasteful carbonylation reactions that employ alcohols and amines as the starting materials and oxygen as the oxidant in the presence of different metal catalysts have been used in the synthesis of organic carbonates and ureas in the last few years (Scheme 3). Enichem and Ube have both achieved the industrial production of dimethyl carbonate (DMC).[27,28]

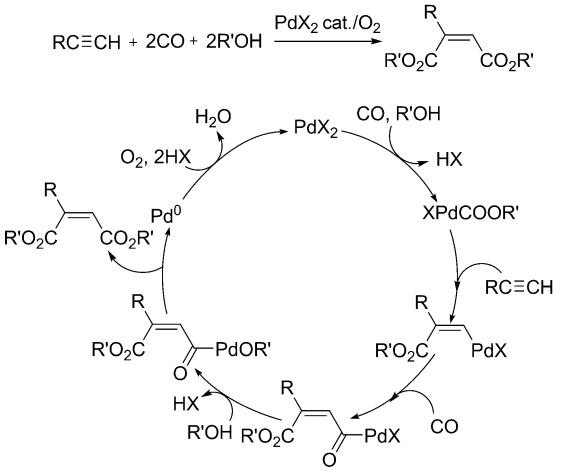


Scheme 3. Synthesis of organic carbonates and ureas through oxidative carbonylation reactions.

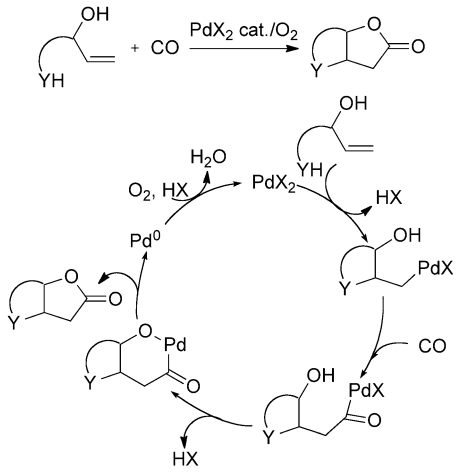
Since it has been fully summarized in several reviews and books,[29–37] we will not discuss this protocol in this review.

Another important type of oxidative carbonylation reaction is the oxidative carbonylation of alkenes and alkynes, which leads to the direct synthesis of structurally diverse acyclic and heterocylic carbonyl products.[12,38–56] Two typical examples are shown in Schemes 4 and 5.

The proposed mechanism shown in Scheme 5 is general understanding for such reactions. An acylic palladium complex is formed by nucleophilic attack at the Pd^{II}-activated unsaturated bond, which subsequently undergoes CO insertion, alcoholysis or aminolysis, and reductive elimination to produce the ester or amide products. For the oxidative carbonylation reactions of unsaturated compounds, the PdI_2/KI catalyst system developed by Gabriele et al. showed high efficiency.[34–36] They proposed that the in situ formed anionic palladium complex $[PdI_4]^{-2}$ was very active. Additionally, the

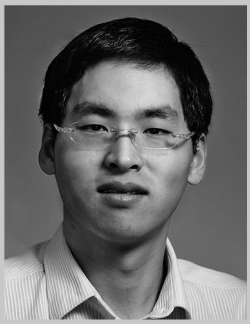


Scheme 4. Oxidative carbonylation reaction of an alkyne.



Scheme 5. Oxidative carbonylation reaction of an alkene.

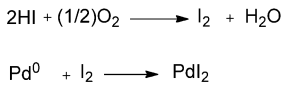
Aiwen Lei received his Bachelors degree (1995) from Huaibei Normal University, and obtained his PhD (2000) from Prof. Xiyan Lu at the Shanghai Institute of Organic Chemistry, Chinese Academy of Sciences. He then moved to Pennsylvania State University as a postdoctoral fellow with Prof. Xumu Zhang. He joined Stanford University (2003) as a research associate with Prof. James P. Collman, and later became a full professor (2005) at the College of Chemistry and Molecular Sciences, Wuhan University.



Qiang Liu was born in 1984, and received his Bachelors Degree of Science in 2007 from Wuhan University, under the supervision of Prof. Aiwen Lei. He joined Prof. Lei's group in 2006, and is currently a 4th year Ph.D. student. He was selected as one of the outstanding young researchers to attend the 60th Lindau Noble Laureates Meeting in 2010. His research interest is the transition metal catalyzed oxidative coupling reactions.

Hua Zhang was born in 1987, and received his Bachelors Degree of Science in 2008 from Wuhan University, under the supervision of Prof. Aiwen Lei. He has joined Prof. Lei's group since 2007, and is currently a 3rd year Ph. D.student. His research focuses on the transition metal catalyzed oxidative coupling reactions.

reoxidation of the Pd^0 species is a facile process in this catalytic system, which involves the oxidation of HI to I_2 followed by oxidative addition of I_2 to Pd^0 to regenerate PdI_2 (Scheme 6).



Scheme 6. Reoxidation for Pd^0 in the PdI_2/KI catalysis system.

Detailed discussions related to these transformations are nicely summarized in several accounts.[12,38–41]

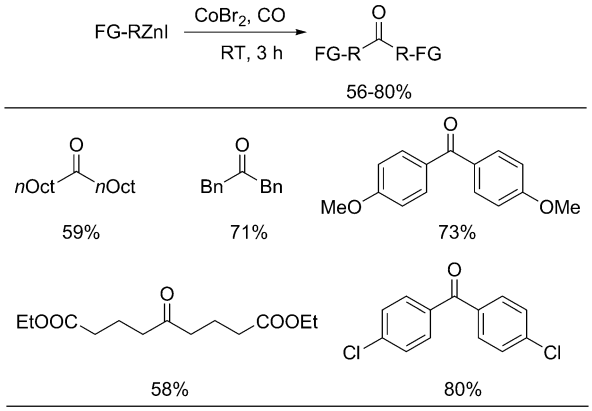
2. Oxidative Carbonylation Reactions with R–M

In recent years, oxidative carbonylation reactions, in which organometallic reagents (R–M) or hydrocarbons (R–H) were employed as the nucleophiles, have been rapidly developed and have significantly enriched the application scope of the oxidative carbonylation transformation. In this perspective, we mainly focus on these oxidative carbonylation reactions.

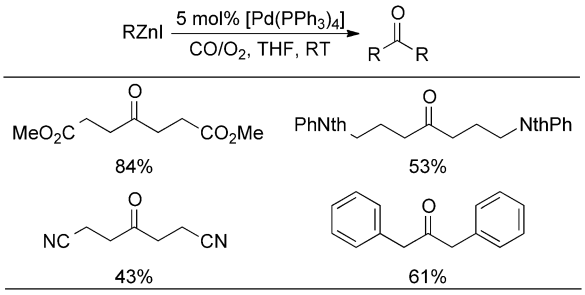
2.1. Oxidative Carbonylation of Organozinc Reagents

In 1995, Knochel et al. reported the oxidative carbonylation of organozinc reagents to produce symmetric ketones in the presence of stoichiometric cobalt bromide (Scheme 7).[57] A series of alkyl and aromatic symmetric ketones were prepared in moderate to good yields.

Subsequently, Jackson et al. reported the palladium-catalyzed oxidative carbonylation of organozinc reagents using O_2 as the oxidant (Scheme 8).[58] This reaction produced symmetric ketones in moderate to high yields, and avoided the requirement of stoichiometric amounts of metal compounds.



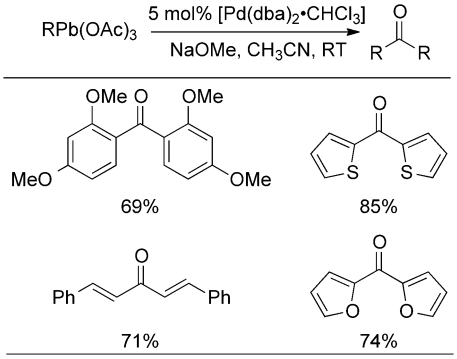
Scheme 7. Stoichiometric $CoBr_2$-mediated oxidative carbonylation of organozinc reagents. Bn = benzyl, FG = functional group.



Scheme 8. Palladium-catalyzed oxidative carbonylation of organozinc reagents. Nth = naphthyl, THF = tetrahydrofuran.

2.2. Oxidative Carbonylation of Organolead Reagents

Organolead reagents were also employed to produce symmetric ketones (Scheme 9).[59] Notably, the organolead compounds acted as both nucleophiles and oxidants, and the authors proposed that $RPb(OMe)_3$ was formed as a key intermediate. A wide range of functional groups including heterocycles were well tolerated in this reaction.

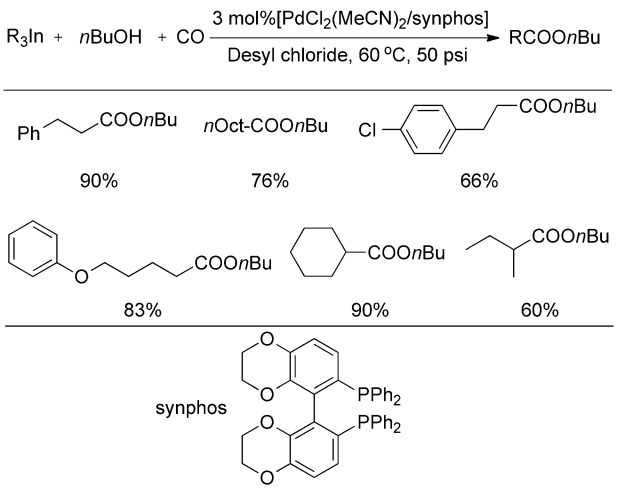


Scheme 9. Palladium-catalyzed oxidative carbonylation of organolead reagents. dba = dibenzylideneacetone.

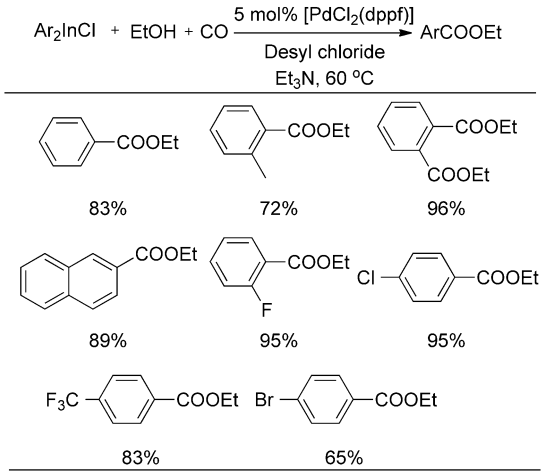
2.3. Oxidative Carbonylation of Organoindium Reagents

Palladium-catalyzed oxidative carbonylation of organometallic reagents to produce esters was originally developed by Lei et al. In 2008, they reported the first example of palladium-catalyzed oxidative carbonylation of organoindium reagents to produce different esters (Schemes 10 and 11).[60] Organoindium reagents are relatively moisture stable and can tolerate the hydroxy group very well. Both alkyl and aryl indium reagents could be converted into the corresponding esters smoothly in good to excellent yields.

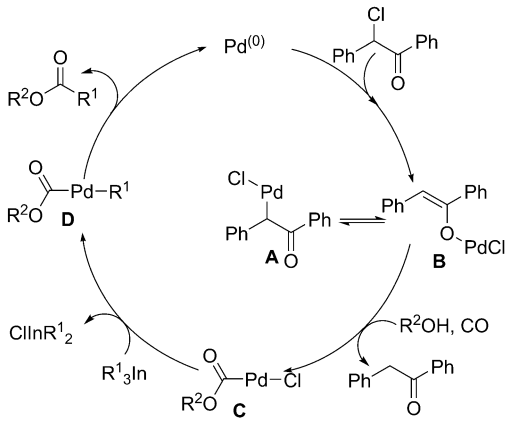
The mechanism proposed in Scheme 12 was investigated by using stoichiometric reactions. Oxidative addition of the Pd^0 species to desyl chloride (**A**) and quick tautomerization provides the Pd^{II} enolate species **B**. The enolate group in **B** is then displaced by ROH with concomitant release of 1,2-diphenylethanone, and subsequent CO insertion gives the alkoxycarbonyl palladium complex **C**, which undergoes trans-



Scheme 10. Oxidative carbonylation of alkylindium reagents.



Scheme 11. Oxidative carbonylation of arylindium reagents. dppf = 1,1′-bis(diphenylphosphanyl)ferrocene.



Scheme 12. Proposed mechanism for the oxidative carbonylation of organoindium reagents.

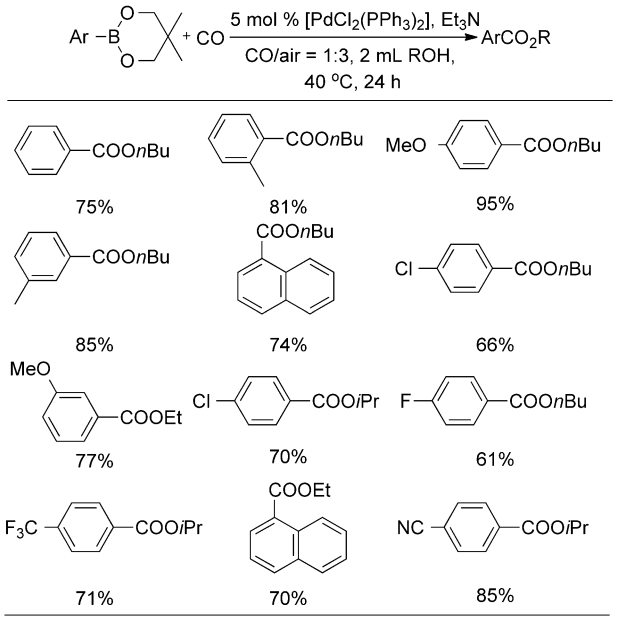
metalation with R_3In and reductive elimination to afford the carbonyl product and regenerate the Pd^0 species.

Although this transformation gave satisfying yields and selectivity, equivalent amounts of the organic oxidant (desyl chloride) was used, thereby producing 1,2-diphenylethanone as a by-product.

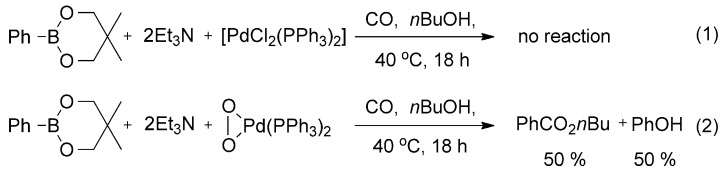
2.4. Oxidative Carbonylation of Organoboronic Reagents

On the basis of their previous work, Lei and co-workers additionally developed the palladium-catalyzed oxidative carbonylation of arylboronic esters using air as an oxidant, under balloon pressure of an air and CO gas mixture (Scheme 13).[61] Arylboronic acid derivatives are air and moisture stable, as well as compatible with a broad spectrum of common functional groups.[62–64] For these reasons, they have been widely applied in chemical syntheses.[65–67] Additionally, the oxidant of this reaction was air, which is the ideal oxidant for oxidative carbonylation, and running the reaction at atmospheric pressure also makes the process operationally applicable. As shown in Scheme 13, various functional groups were well tolerated in this reaction.

The preliminary mechanism of this reaction was explored by using stoichiometric reactions. In the presence of CO gas, two stoichiometric experiments revealed the different transmetallation reactivities of $[PdCl_2(PPh_3)_2]$ and $[(\eta\text{-}O_2)Pd(PPh_3)_2]$ complexes with phenylboronic ester. No biphenyl or any carbonylation products were detected in the reaction of phenylBneop (Bneop = neopentylglycolatobory with $[PdCl_2(PPh_3)_2]$ when using NEt_3 as the base [Scheme 14, Eq. (1)]. In fact, the starting phenylBneop was quantitatively recovered. However, when $[PdCl_2(PPh_3)_2]$ was replaced by $[(\eta\text{-}O_2)Pd(PPh_3)_2]$, 50% *n*-butyl benzoate and 50% phenol were obtained [Scheme 14, Eq. (2)]. These comparative results indicated that the transmetallation reaction could only occur between phenylBneop and $[(\eta\text{-}O_2)Pd(PPh_3)_2]$ under these reaction conditions; $[PdCl_2(PPh_3)_2]$ as the catalyst precursor needs to be converted into $[(\eta\text{-}O_2)Pd(PPh_3)_2]$ to initiate the catalytic cycle.

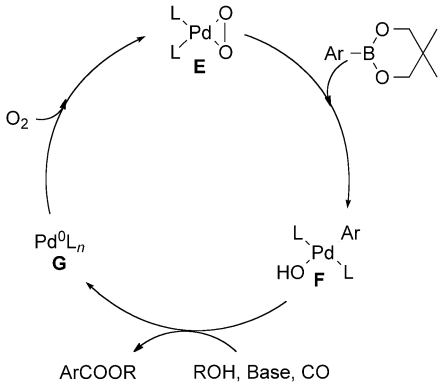


Scheme 13. Oxidative carbonylation of arylboronic esters.



Scheme 14. Reactions run with stoichiometric amounts of the reagents.

A proposed catalytic cycle of this aerobic oxidative carbonylation is described in Scheme 15. A fast transmetallation between the $[(\eta\text{-}O_2)Pd(PPh_3)_2]$ complex **E** and PhBneop generates the *trans*-$[PhPd(OH)(PPh_3)_2]$ complex **F**.[68] Carbonylation of complex **F** in the presence of CO, ROH, and a base results in the product ArCOOR, and the Pd^0Ln species **G**. The $[(\eta\text{-}O_2)Pd(PPh_3)_2]$ complex **E** could be regenerated from the reaction of Pd^0Ln with O_2.

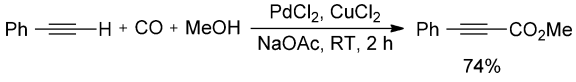


Scheme 15. Proposed mechanism for the oxidative carbonylation of arylboronic esters.

3. Oxidative Carbonylation Reactions with R–H

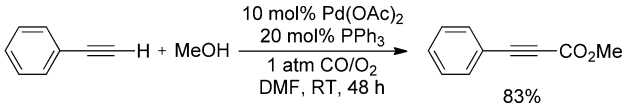
3.1. Oxidative Carbonylation Reactions of Alk-1-ynes

2-Alkynoates constitute an important class of compounds as biologically active substances and as versatile intermediates in organic synthesis of biologically important molecules.[69–71] Traditional preparation of alkynecarboxylates involves lithiation of 1-alkynes and subsequent quenching with chloroformate. However, this method requires the use of a strong base. Oxidative carbonylation of alkynes with alcohols affording alkyl 2-alkynoates with retention of the triple bond has been developed as a convenient method for catalytically synthesizing these alkynoates. $PdCl_2$-catalyzed carbonylation of 1-alkynes using NaOAc as base in the presence of a Cu^{II} salt as the oxidant was first reported by Tsuji (Scheme 16).[72] Other oxidants such as quinones have also been used to perform the carbonylation of phenylacetylene.[73,74]



Scheme 16. Alkoxycarbonylation of 1-alkynes using $CuCl_2$ as the oxidant.

In 2004, Yamomoto et al. developed a new method to produce alkyl 2-alkynoates from 1-alkynes in alcohol with CO (one atmosphere) at room temperature using palladium/phosphine catalysts and molecular oxygen as an oxidant (Scheme 17).[75] On the basis of the behavior of model complexes such as methoxycarbonylpalladium and alkynylpalladium complexes, they proposed a mechanism to account for this carbonylation reaction. Methyl 2-alkynoates and a Pd^0 species were generated through reductive elimination of the intermediate coordinated by the methoxycarbonyl and alkynyl groups. The oxidation of Pd^0 into a Pd^{II} species in the presence of a halide ion was confirmed to proceed cleanly with molecular oxygen as the oxidant.

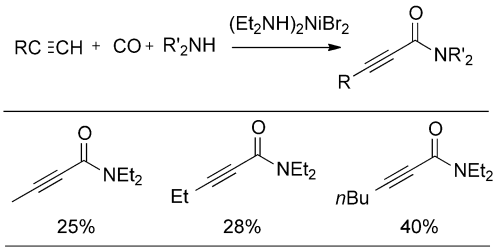


Scheme 17. Alkoxycarbonylation of 1-alkynes using O_2 as oxidant. DMF = *N*,*N*′-dimethylformamide.

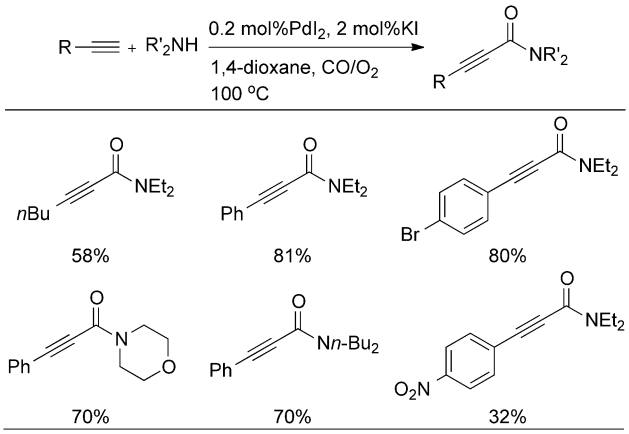
2-Ynamides are useful intermediates for the synthesis of many biologically active molecules and heterocyclic compounds.[76,77] Traditional methods for the preparation of 2-ynamides include the Pd/Cu-catalyzed coupling reaction between alk-1-ynes and carbamoylchlorides.[76–78] As an alternative approach to synthesizing 2-ynamides, direct aminocarbonylation of alk-1-ynes is more synthetically attractive. However, although the catalytic oxidative carbonylation of alk-1-ynes with alcohols to obtain alkynylesters has been known for years, very few analogous oxidative aminocarbonylations have been described.

Oxidative aminocarbonylation of alk-1-ynes has been achieved in the presence of stoichiometric amount of nickel[79,80] (Scheme 18). The reaction yields were low and selectivities were not ideal.

The first catalytic aminocarbonylation of alk-1-ynes was accomplished by Gabriele et al.[81] Both alkyl- and arylacetylenes could be converted to the corresponding 2-ynamides successfully, and the latter were more reactive substrates (Scheme 19). Moreover, reactions employing alkylacetylenes also generated small amounts of by-products resulting from oxidative diaminocarbonylation of the triple bond. Employing a nucleophilic secondary amine such as diethylamine as the substrate was vital for the reaction. Sterically hindered amines (e.g., diisopropylamine) or amines with low basicity



Scheme 18. Nickel-mediated oxidative aminocarbonylation of alk-1-ynes.

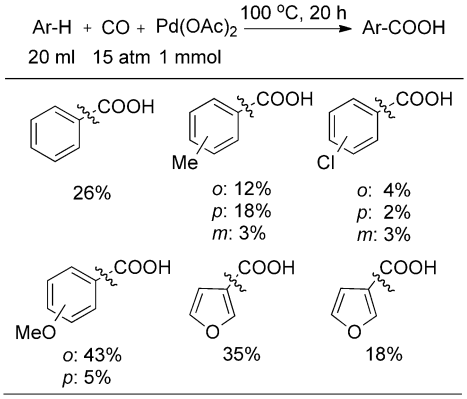


Scheme 19. Palladium-catalyzed oxidative aminocarbonylation of alk-1-ynes.

(e.g., *N*-methylaniline) were inert in this reaction. In addition, the reactions of primary amines led to complex reaction mixtures. The main products, ureas in this case, resulted from oxidative carbonylation of the amino group. This methodology has been successfully applied to the direct synthesis of a variety of carbonylated heterocycles starting from terminal alkynes bearing a suitably placed nucleophilic group.[82–88]

3.2. Oxidative Carbonylation Reactions of Simple Arenes

Direct oxidative carbonylation of arenes was pioneered by Fujiwara et al.[89] They first reported the synthesis of aromatic acid derivatives directly from simple arenes and carbon monoxide in the presence of a stoichiometric amount of palladium diacetate (Scheme 20).[90] In the proposed mechanism, aromatic compounds undergo palladation to give the aromatic–Pd α complex, which further reacts with carbon monoxide to produce an acyl palladium species. The newly formed palladium species then undergoes reductive elimination to generate the Pd^0 species and acetic benzoic anhydride, which additionally reacts with acetic acid to afford the final product benzoic acid. The reaction delivered *ortho*- and *para*-substituted products when an electron-donating group was attached to the aromatic ring. The electron-rich substrates were more active in this reaction, thus indicating that C–H activation occurred through electrophilic attack of the Pd^{II}

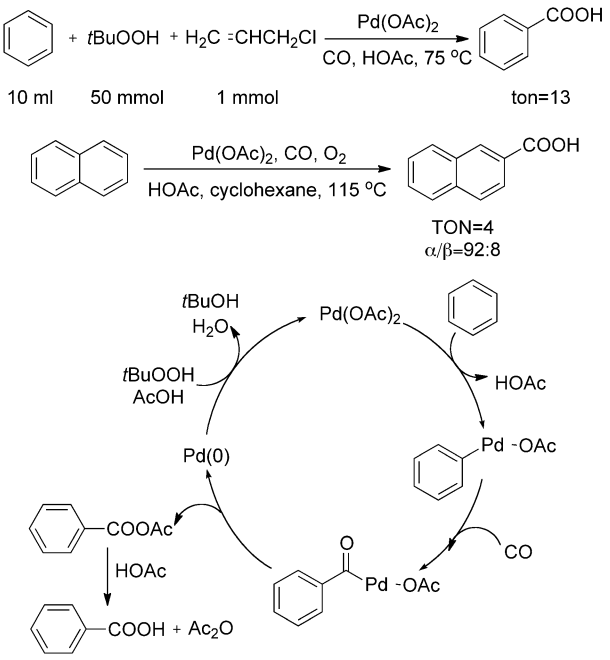


Scheme 20. Stoichiometric amounts of $Pd(OAc)_2$ for mediation of the oxidative carbonylation of simple arenes. The reported yields are based on $Pd(OAc)_2$.

species on the arenes. This step is also the rate-limiting step of the reaction.

Subsequently, Fujiwara et al. improved the above-mentioned stoichiometric reaction and developed a catalytic reaction involving the $Pd(OAc)_2$-catalyzed oxidative carbonylation of simple arenes with CO by direct C–H activation (Scheme 21).[91–93] The mechanism is analogous to the stoichiometric reaction and the Pd^{II} species was regenerated by the oxidant, *tert*-butyl hydroperoxide.

Furthermore, to improve the reaction efficiency, Fujiwara et al. developed a more powerful catalytic system. A series of simple arenes such as benzene, toluene, chlorobenzene, anisole, and naphthalene were oxidatively carboxylated by $Pd(OAc)_2$ in the presence of potassium peroxodisulfate as the

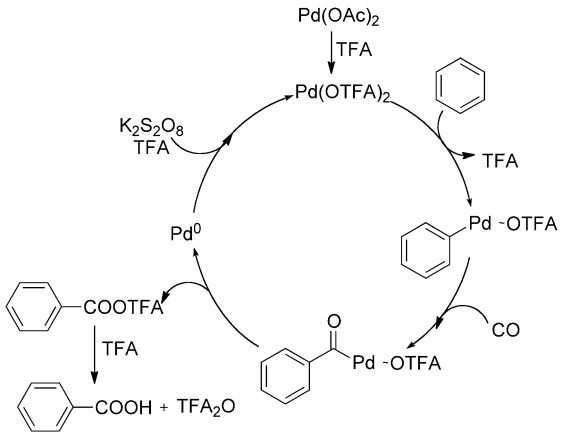


Scheme 21. $Pd(OAc)_2$ catalyzed oxidative carbonylation of simple arenes.

oxidant in trifluoroacetic acid (TFA) at room temperature under an atmosphere of CO. The aromatic carboxylic acids were formed in good yields (Scheme 22).[94,95]

The author proposed that $Pd(OAc)_2$ reacted with trifluoroacetic acid (TFA) first to generate $Pd(OTFA)_2$ having a more electron-deficient palladium center. As mentioned above, the mechanism of C–H activation in this kind of reaction involves electrophilic attack of aromatic ring by the Pd^{II} species. Therefore, the more electron-poor Pd^{II} species, $Pd(OTFA)_2$, would facilitate this process and make it possible to react under mild reaction conditions (room temperature).

Recently, Ishii and co-workers developed the $Pd(OAc)_2$/molybdovanadophosphate-catalyzed oxidative carboxylation of anisole derivatives with O_2 as the oxidant. Using O_2 as the oxidant is more environmentally friendly than using *tert*-butylhydroperoxide or potassium peroxodisulfate (Scheme 23).[96] In addition, phenol also performed well in this reaction. *Ortho*- and *para*-hydroxybenzoic acid were obtained in 90:10 selectivity at 90% conversion for the reaction of phenol. However, benzene is inert to this reaction, giving trace amounts of benzoic acid (<5%). The proposed reaction mechanism is similar to that proposed by Fujiwara et al. The only difference is that the oxidant was changed from a stoichiometric amount of peroxide to a catalytic amount of molybdovanadophosphate and oxygen.

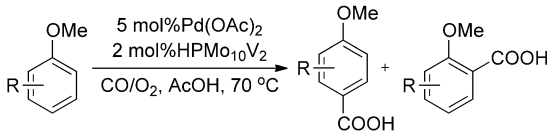


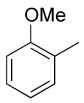
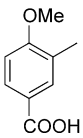
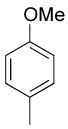
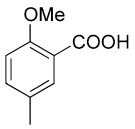
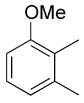
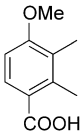
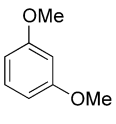
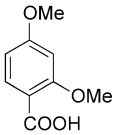
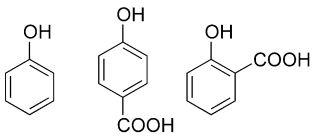
Scheme 22. $Pd(OAc)_2$/TFA-catalyzed oxidative carbonylation of simple arenes.

3.3. Oxidative Carbonylation Reactions of Arenes Bearing Directing Groups

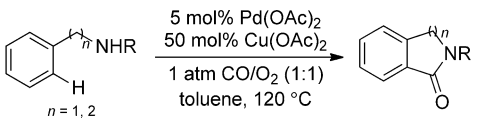
In 2004, Orito reported the Pd^{II}-catalyzed direct carbonylation of secondary ω-arylalkylamines, such as *N*-alkylbenzylamines or *N*-alkylphenethylamines, to afford a variety of five- or six-membered benzolactams (Scheme 24).[97] Catalytic amounts of $Pd(OAc)_2$ and $Cu(OAc)_2$ were employed under a mixed atmosphere of CO and air. The carbonylation reaction was proposed to proceed with *ortho* palladation, which induced remarkable site selectivity.

Yu and co-workers subsequently reported the Pd^{II}-catalyzed direct carboxylation of benzoic and phenylacetic acid derivatives to form dicarboxylic acids (Scheme 25).[98] The reaction conditions were also applicable for the carboxylation of vinyl C–H bonds. Notably, the first C–H insertion complex,



Substrate	Product	Conv. [%]	Selectivity [%]
		90	73
		49	64
		90	75
		89	92
	90 : 10	90	59

Scheme 23. $Pd(OAc)_2/HPMo_{10}V_2$-catalyzed oxidative carbonylation of anisole.

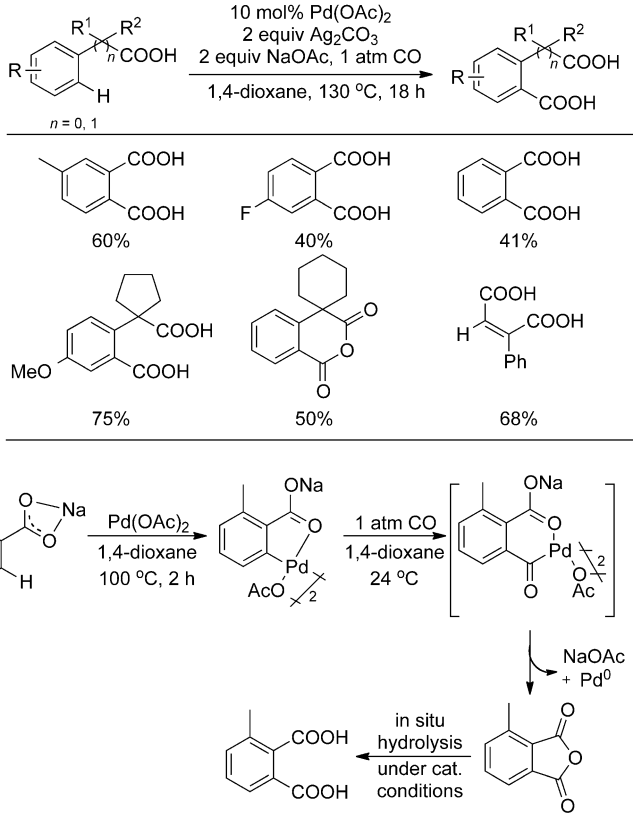


Scheme 24. $Pd(OAc)_2$-catalyzed oxidative carbonylation of secondary ω-arylalkylamines.

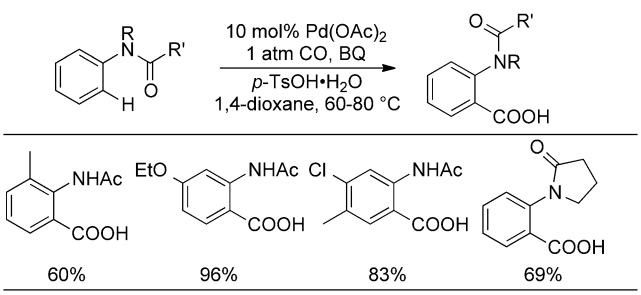
Pd–aryl, from carboxylic acids was characterized by X-ray crystallography.

Very recently, they further developed the Pd^{II}-catalyzed *ortho* carboxylation of anilides to form *N*-acyl anthranilic acids (Scheme 26).[99] The transformation provided a novel and efficient strategy for the rapid assembly of biologically and pharmaceutically significant molecules, such as benzoxazinones and quinazolinones, from simple anilides without introducing and removing an external directing group. A monomeric palladacycle containing *p*-toluenesulfonate as an anionic ligand was characterized by X-ray crystallography.

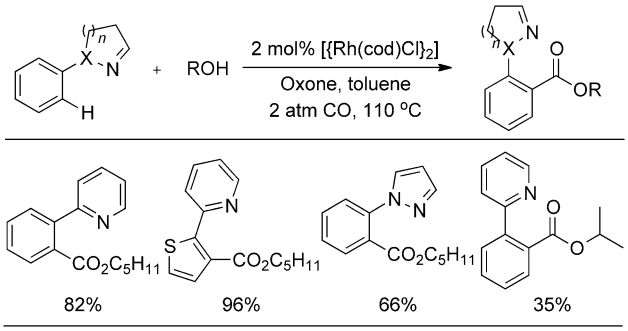
Zhang and co-workers described the rhodium-catalyzed *ortho* carbonylation of 2-arylpyridines to form the corresponding esters (Scheme 27).[100] A broad substrate scope has been demonstrated allowing carbonylation of electron-rich, electron-poor, and heterocyclic arenes with broad functional-group tolerance and excellent regioselectivity.



Scheme 25. $Pd(OAc)_2$-catalyzed oxidative carbonylation of benzoic and phenylacetic acid.

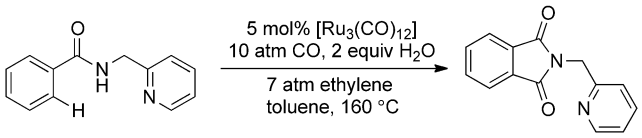


Scheme 26. Palladium-catalyzed *ortho*-carboxylation of anilides. cod = 1,5-cyclooctadiene.



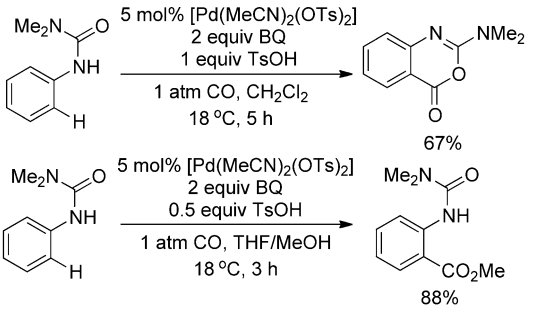
Scheme 27. Rhodium-catalyzed *ortho*-carboxylation of 2-arylpyridines.

Ruthenium-catalyzed intramolecular oxidative carbonylation of the *ortho* C–H bonds in aromatic amides, in which the pyridin-2-ylmethylamino moiety acted as a bidentate directing group, was achieved.[101] The presence of ethylene as a hydrogen acceptor and H_2O, probably for the generation of an active catalytic species, was required. A wide variety of functional groups, including methoxy, amino, ester, ketone, cyano, chloro, and even bromo substituents, were well tolerated (Scheme 28).



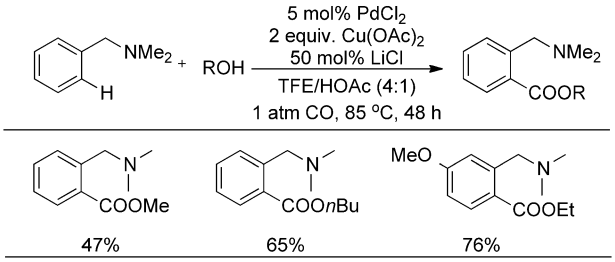
Scheme 28. Ruthenium-catalyzed oxidative carbonylation of aromatic amides.

Urea-directed carbonylation of aromatic C–H bonds proceeded efficiently at 18 °C under 1 atm of CO with 5 mol% $[Pd(OTs)_2(MeCN)_2]$ as the precatalyst and benzoquinone as the oxidant.[102] In CH_2Cl_2, cyclic imides were obtained in high yields whereas anthranilates were formed when a mixture of THF/MeOH was employed as the solvent. The latter were proposed to be the result of solvolytic ring opening of the imides with MeOH (Scheme 29).



Scheme 29. Palladium(II)-catalyzed oxidative carbonylation of urea compounds.

Recently, Shi et al. developed a highly regioselective carbonylation of substituted *N*,*N*-dimethylbenzylamines catalyzed by $PdCl_2$ with the assistance of LiCl.[103] The preformed *N*,*N*-dimethylbenzylamine could be further converted into *ortho*-alkyl benzoate under mild conditions. These two transformations could be combined into a one-pot procedure to give the desired product in moderate yield. In addition, synthesis of variolaric acid fragments was achieved by employing this methodology (Scheme 30).



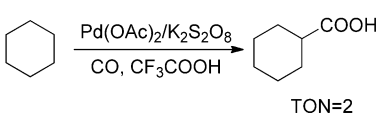
Scheme 30. $PdCl_2$-catalyzed oxidative carbonylation of *N*,*N*-dimethylbenzylamines. TFE = trifluoroenthanol.

3.4. Oxidative Carbonylation Reactions of Alkanes

Direct functionalization of alkanes through C–H activation has attracted great interest because alkanes, particularly methane, are one of the most abundant natural sources of organic molecules.[104–106] Alkane activation/functionalization remains challenging since it is difficult to cleave the C–H bond selectively while keeping the functionalized product less reactive than the starting material under the same reaction conditions.[107–111] Accordingly, the activation and functionalization of small alkane molecules, such as methane, will affect chemical synthesis profoundly from both an industrial and academic points of view.[112–116]

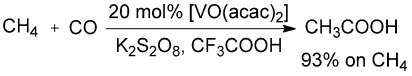
Fujiwara et al. reported the first palladium-catalyzed oxidative carbonylation of alkanes in 1989 as shown in Scheme 31.[117] The author proposed that the mechanism of this C–H activation of the alkane was electrophilic substitution with a Pd^{II} species to form an alkyl Pd^{II} complex.

Subsequently, Fujiwara et al. reported direct catalytic conversion of methane and CO into acetic acid by the Pd/$Cu(OAc)_2$/$K_2S_2O_8$, $Cu(OAc)_2$/$K_2S_2O_8$,[118–124] and $Yb(OAc)_3$/$Mn(Ac)_2$/NaClO[125] catalytic systems. Acetic acid synthesis from methane and CO reported by Olah et al. and Hogeveen et al. made use of magic acids.[125,126] Moreover, $K_2S_2O_8$-assisted $RhCl_3$- and vanadium-catalyzed carbonylations of methane with CO were reported by Shul'pin et al. and Sen and Lin.[127–129] However, the yields of acetic acid based on methane in the above mentioned reactions were not satisfactory.



Scheme 31. $Pd(OAc)_2$-catalyzed oxidative carbonylation of alkanes.

Later on, Fujiwara et al. made a breakthrough in this field. They developed highly efficient vanadium-[130] and calcium-catalyzed[131] oxidative carbonylation of alkanes that proceeded in high yields based on methane. The $[VO(acac)_2]$ catalyst in the presence of $K_2S_2O_8$ and CF_3COOH could efficiently convert methane and CO into acetic acid with high selectivity. The reaction of methane (5 atm) with CO (20 atm) at 80 °C for 20 hours gave acetic acid in 93 % yield based on methane (Scheme 32). Other vanadium compounds such as V_2O_3, V_2O_5, and $NaVO_3$ and various vanadium-containing heteropolyacids such as $H_5PV_2Mo_{10}O_{40}$, $H_4PVW_{11}O_{40}$, and $H_5SiVW_{11}O_{40}$, also worked well as catalysts.

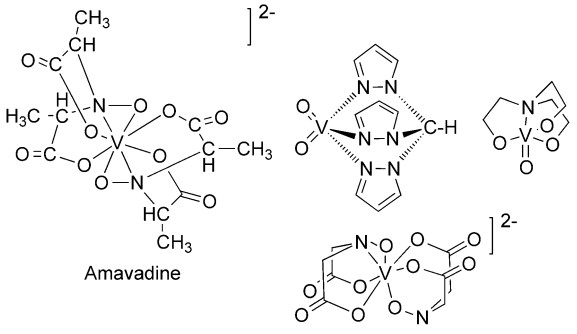


Scheme 32. Vanadium-catalyzed oxidative carbonylation of methane. acac = acetylacetonate.

It was presumed that the high oxidation state oxovanadium species V^V=O could abstract an H· from CH_4 to form CH_3·, which could then react with CO to give CH_3CO·. The formed acetyl radical would be further oxidized by V^V=O to give the acetyl cation CH_3CO^+, which could then be quenched with OH^- to generate the final product acetic acid.

Fujiwara et al. also found that using calcium chloride as the catalyst instead of vanadium provided excellent results. It is also a radical process as tested by radical trap experiments.[131]

Very recently, Pombeiro and co-workers synthesized a series of vanadium(IV or V) complexes with N,O- or O,O-ligands such as amavadine (Scheme 33); these complexes were found to be excellent catalysts for the efficient single-pot conversion of methane into acetic acid in trifluoroacetic acid (TFA) using peroxodisulfate as the oxidant.[132–138] TFA acted as a carbonylating agent and CO was an inhibitor for some systems, although for others there was an optimum CO pressure. With amavadine as the catalyst, methane could be converted into acetic acid even in the absence of CO.[138] The most effective catalysts bearing triethanolaminate or (hy-



Scheme 33. Typical vanadium catalysts for the oxidative carbonylation of alkanes.

droxyimino) dicarboxylates produced CH_3COOH in more than 50% yields (based on CH_4) and remarkably high turnover numbers (TONs) of up to 5.6×10^3. The catalyst could also remain active upon multiple recycles, which showed its potential applicability. These carboxylations were presumed to proceed through a free-radical mechanism, which was tested by both radical trap experiments and DFT calculations. The calculations also indicated that peroxodisulfate behaved as both a source of sulfate radicals, which were initial methane H abstractors, and as a peroxidative oxidizing agent for vanadium.[125]

4. Summary and Outlook

To summarize, we have reviewed the oxidative carbonylation reactions that use organometallic reagents (R–M) and hydrocarbons (R–H) as nucleophiles. Such reactions provide a novel and efficient tool for constructing a diversity of carbonylative compounds. However, challenges still remain in this rapidly developing area. For most of the reactions, noble metals, including palladium, rhodium, and ruthenium, are still essential for serving as catalysts. Reactions that only involve cheap metal catalysts as well those that have increased TONs are attractive yet challenging. Moreover, there is no doubt that the oxidant is crucial in the reactions and obviously oxygen or hydroperoxide would be the green and ideal choice. Additionally, the reaction pressure is normally above 1 atm. Significant efforts should be made to lower the pressure to 1 atm for large-scale production, especially for the dangerous CO and O_2 gas mixture. In contrast, the most ideal bond-formation mode, direct C–H activation of R–H as the nucleophile, has not yet been achieved with high selectivity without the assistance of a directing group. Therefore, development of catalytic system with higher efficiency, selectivity, and larger substrate scope is an important issue for this transformation. In addition, it will be necessary to study in more detail the mechanistic aspects of the oxidative carbonylation reaction. This aspect will require more work to gain a clearer understanding of the reaction. Above all, the oxidative carbonylation reaction will remain a hot research area because of both its advantages and challenges. In the near future, oxidative carbonylation should be an extraordinarily powerful approach towards the synthesis of carbonylated compounds.

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