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Palladium-Catalyzed Carbonylative Transformation of C(sp^3)−X Bonds

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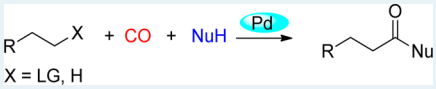
ABSTRACT: During the last 50 years, the palladium-catalyzed carbonylation reactions underwent continuous development. Apart from carbonylation of aromatic (pseudo)-halide and alkene (C-sp^2) compounds, the use of C(sp^3)−X compounds such as allyl compounds, benzyl compounds, and aliphatic alkanes have become the most useful tool for the synthesis of β,γ-unsaturated carbonyl compounds, aliphatic carboxylic acid, and their derivatives. The recently budding development in the area of palladium-catalyzed C(sp^3)−X (especially X = H) activation makes us feel it necessary to file a summary on the past, current contributions, and a prospective outlook on the palladium-catalyzed carbonylative transformation of C(sp^3)−X bonds, which is the focus of this review.



KEYWORDS: *palladium catalyst, carbonylation, C(sp^3)−X bonds, cross-coupling, carbon monoxide*

1. INTRODUCTION

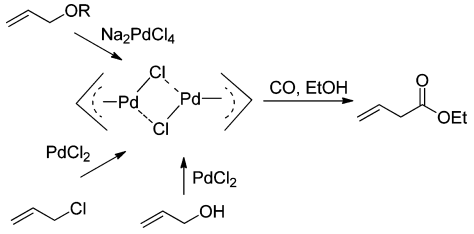
Palladium-catalyzed cross-coupling reactions have become one of the most powerful tools for the synthesis of novel bioactive compounds and advanced materials.[1] Incorporation of carbon monoxide, the so-called carbonylative coupling reactions, were also well studied during the last 50 years and provided a new approach for constructing a synthetically versatile carbonyl group with high efficiency and selectivity.[2] While carbonylation of C(sp^2)−X (aryl; vinyl (pseudo) halides and activated C−H compounds) were well studied and in some cases already industrially applied, the carbonylative coupling of C(sp^3)−X (alkyl halides, alkyl C−H bond) received relatively fewer investigations.[3] The problem is because CO is a strong π-acidic ligand, which will render a low-valent palladium species relatively electron deficient. This increases the difficulty of oxidative addition of C−X toward palladium(0).[2b,4] Besides, side-reactions like β-hydrogen elimination and nonproductive reductive elimination may take place, too. To avoid these problems, a serial of catalytic systems had been developed mainly before 2000. After years of stillness, the flourishing development of C−H bonds activation stimulated chemists to revisit the carbonylative transformation of C(sp^3)−X bonds. To our surprise, there is no general description of palladium-catalyzed carbonylative transformation of C(sp^3)−X bonds in existence. Herein we would like to file the palladium-catalyzed carbonylation of C(sp^3)−X compounds. Our goal is to make a connection of the past contributions and current development. The text is organized according to the substrates that were used.

2. ALLYL COMPOUNDS

Allyl compounds are typically activated C(sp^3)−X compounds. In spite of the tremendous progress in nucleophilic allylic substitution reactions, carbonylation of allyl compounds has received relatively less attention. Carbonylation of allylic compounds offers attractive tools to synthesize β,γ-unsaturated carbonyl compounds,[5] which are versatile building blocks. A general accepted mechanism in this topic starts with the oxidative addition of allylic compounds to palladium(0) complexes and forms the π-allylpalladium complexes and then carbon monoxide insertion to form the acyl palladium species; after reacting with different nucleophiles the final products are observed. Here carbonylation reactions with different allyl substrates are presented.

2.1. π-Allylpalladium Compounds. In 1963, Tsuji, Kiji, and Morikawa[6] reported the stoichiometric synthesis of ethyl 3-butenoate by the reaction of the π-allylpalladium chloride complex with carbon monoxide in ethanol. Soon, they found that a catalytic amount of palladium chloride could also promote this reaction using allylic chloride, allylic alcohol,[6] allylic ether, and ester as substrates (Scheme 1).[7,8]

Scheme 1. Synthesis of the π-Allyl Complex and Its Carbonylation



π-Allylpalladium species could also be used as catalyst; for example, Whitfield and co-workers discovered the π-allylpalladium chloride complex could catalyze the reaction between allylic halides and carbon monoxide, and high yields (up to 94%) of alk-3-enoyl chlorides were achieved (Scheme 2).[9] In 1969, Medema, Helden, and Kohll reported their detailed kinetic study on this transformation.[10]

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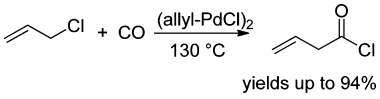
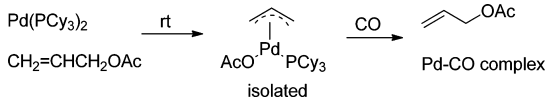
Scheme 2. π-Allylpalladium Complex-Catalyzed Carbonylation of Allyl Chloride



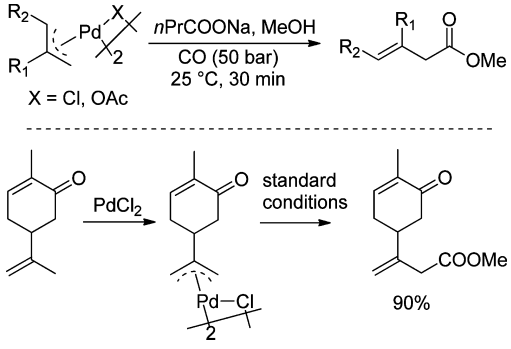
Yamamoto and co-workers[11] reported in 1981 their results on the synthesis of η^3-allyl(acetato)palladium-type of complexes start from allyl acetate and $Pd(PCy_3)_2$. They applied this complex with carbon monoxide and found the reductive elimination of allyl acetate from the complex took place instead of the CO insertion, which illustrated the challenge in carbonylation reactions of allyl acetates (Scheme 3).

Scheme 3. Challenge in the Carbonylation of Allyl Acetates



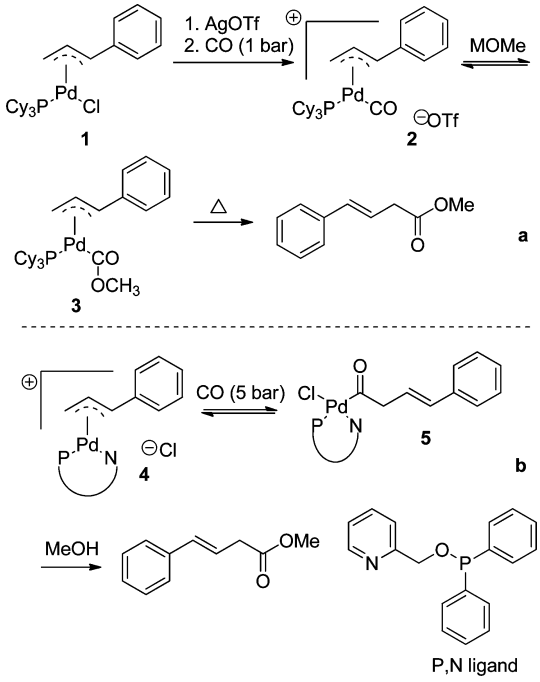
In the early stage of allyl compounds carbonylation reactions, the pressures of carbon monoxide were very high; for example, in Whitfield's system, 500 bar of carbon monoxide was needed. In 1982, Milstein[12] reported a stoichiometric carbonylatlon of (π-allyl) palladium complexes; the addition of an extra amount of carboxylic acid anions (sodium butyrate was found to be the best additive) allowed the reaction to take place under milder conditions (50 bar CO). High regioselectivity at the less steric hindered terminal allylic carbon was observed (Scheme 4). In the absence of sodium butyrate, decomposition of the chloro-bridged complexes took place without formation of any products.

Scheme 4. Room Temperature, Low Pressure Carbonylation of (π-Allyl) Palladium and Its Application



Van Leeuwen did some NMR experiments and characterized several putative intermediates in order to clarify the reaction mechanism.[13] Based on their findings, two possible reaction mechanisms were proposed: associative mechanism at low pressure of CO and an insertion mechanism at high pressure. The author first synthesized (ligand)Pd(cinnamyl)Cl complexes **1** and treated it with 1 bar carbon monoxide and silver triflate affording compound **2** which contained a η^3-cinnamyl group and a coordinated CO ligand. Addition of MeO^- to complex **2** led to the formation of the novel carbomethoxy complex **3** quantitatively. They found that the cinnamyl group was still bonded to palladium in a η^3-fashion (path a, Scheme 5). Then compound **4** was synthesized with a *P-N* ligand in

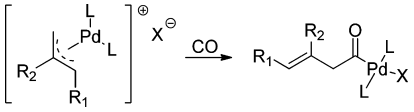
Scheme 5. (a) Associative Mechanism at Low Pressure and (b) Insertion Mechanism at High Pressure



order to stabilize the acyl-palladium compound. At elevated CO pressure and ambient temperature, NMR analysis showed the formation of the insertion product **5** which confirmed an insertion mechanism (path b, Scheme 5).

On the contrary, experimental studies by Osawa and Yamamoto[11,14] showed that the insertion mechanism was responsible for the formation of a η^3-allyl(acetato)palladium species at either atmospheric or higher pressure. They also found that the ligand coordination number as well as the counteranion had effects on the carbon monoxide insertion step. Facile CO insertion into the Pd–allyl bond was observed with a Pd center coordinated with two PMe_3 ligands, while (η^3-2-MeC_3H_4)Pd(Cl)(PMe_3) with one PMe_3 ligand is totally inactive. Besides, there was no carbon monoxide insertion observed when BF_4^- was used as a counteranion (Scheme 6).

Scheme 6. Insertion of Carbon Monoxide into Allylpalladium



2.2. Allyl Halides. A palladium-catalyzed, atmospheric pressure carbonylation of allylic halides under alcohol-potassium carbonate (liquid–solid) two-phase conditions was reported by Kiji and Fukui in 1996.[15] They found that phosphine-free compounds such as $Pd(OAc)_2$ and $Na_2[PdCl_4]$ were convenient catalysts for this transformation. In their system, the presence of triphenylphosphine retarded the carbonylation. Specific allyl chlorides derivated from terpenic olefins were used as substrates by Karim and co-workers.[16]

Amide synthesis from allyl halides with amines and carbon monoxide was reported by Troisi and colleagues in 2010.[17] Probably due to the higher nucleophilicity of amines, side products like monoallylation and double-allylation of amines

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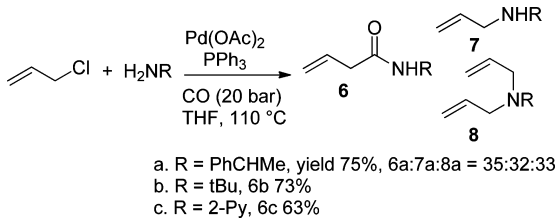
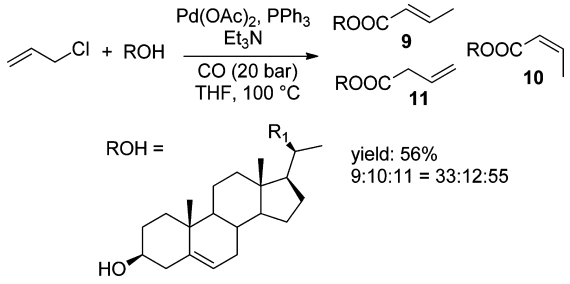
were observed except those with large steric substitute (Scheme 7).

Scheme 7. Amides Synthesis from Allyl Halides with Amines and Carbon Monoxide



Troisi[18a] also demonstrated the alkoxycarbonylation reaction of allyl chloride with some biological relevant alcohols as shown in Scheme 8. The carbonylative transformation of allyl halides

Scheme 8. Synthesis of *O*-Protection of Biologically Relevant Molecules

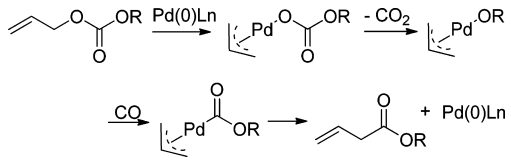


with tin reagents was established by Stille in the early 1980s,[18b−e] but because of the high toxicity of tin, under the guideline of green chemistry, organic chemists are reluctant to apply these reagents in new methodology development. Hence, we will not discuss them in detail here.

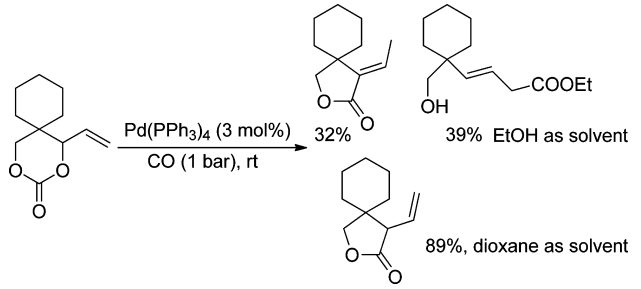
2.3. Allyl Carbonates, Allyl Phosphates. In the case of palladium-catalyzed carbonylation reactions with allyl carbonates and allyl phosphates, as the formation of (π-allyl) palladium complex are much easier, usually those reactions were run at lower temperature (<50 °C). Tsuji et al.[19] reported the palladium-catalyzed decarboxylation-carbonylation of allylic carbonates to form β,γ-unsaturated esters. The reaction proceeded well under atmospheric pressure of carbon monoxide at 50 °C, higher temperature even reduced the yield (Scheme 9).

Similar to Tsuji's strategy, Tamaru and Yoshida reported the palladium-catalyzed decarboxylation-carbonylation of 3-vinyl-1-oxo-2,6-dioxacyclohexanes to synthesis 2-vinyl-γ-butyrolactones.[20] This reaction was found very solvent dependent; products distribution is shown in Scheme 10.

Scheme 9. Palladium-Catalyzed Decarboxylation-Carbonylation of Allylic Carbonates To Form β,γ-Unsaturated Esters

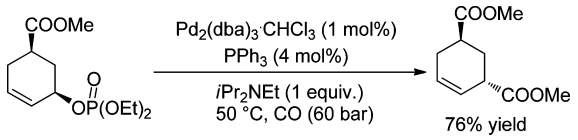


Scheme 10. Solvent-Dependent Transformation of 3-Vinyl-1-oxo-2,6-dioxacyclohexanes



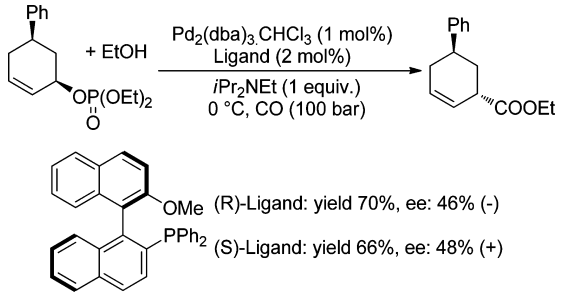
In 1988, Murahashi reported the palladium-catalyzed carbonylation of allyl phosphates to produce β,γ-unsaturated esters in moderate to good yields.[21] Interestingly an example of stereoselectively synthesis of diester was achieved starting from the corresponding phosphate (Scheme 11).

Scheme 11. Palladium-Catalyzed Carbonylation of Allyl Phosphates



Asymmetric alkoxycarbonylation of allyl phosphates in the presence of a chiral monodentate phosphine ligand proceeded very well even at 0 °C.[22] In the case of *cis*-allyl phosphates, about 99% *trans*-products were obtained with moderate ee (enantiomeric excess). The opposite enantiomer could also be obtained by choosing chiral ligand enantiomer (Scheme 12).

Scheme 12. Asymmetric Alkoxycarbonylation of Allylic Phosphate



Apart from the asymmetric version, the applications of allyl phosphate carbonylation in tandem reactions were also reported. In 1993, Torii reported the palladium-catalyzed carbonylative [2 + 2] cycloaddition of allyl diethyl phosphates with imines to produce useful β-lactams.[23] The acyl intermediate **14** involves highly acidic α-proton close to carbonyl which could be abstracted in the presence of base and provide the corresponding more reactive ketene or carbanion derivatives. The in situ formed ketene or carbanion derivatives would react with imine to give rise to the 4-membered ring lactams. For the substrates scope, when imines with conjugated carbonyl such as a ketone or an ester group were used, *cis*-β-lactams were stereoselectively produced at room temperature. Imines without conjugated carbonyl group

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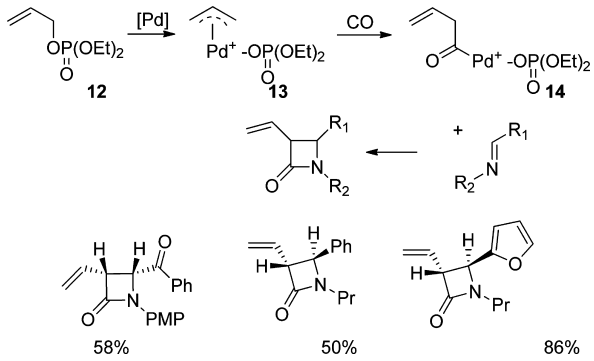
resulted in *trans*-β-lactam at 70 °C (Scheme 13). Though the reaction of allylic phosphate gave β-lactams in good yields, the

Scheme 13. Palladium-Catalyzed Carbonylative [2 + 2] Cycloaddition of Allyl Diethyl Phosphates with Imines[a]

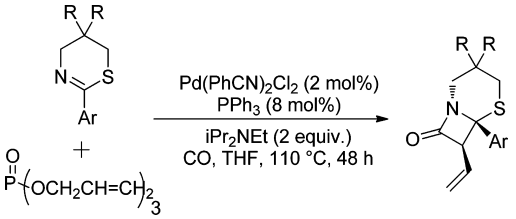


[a] $Pd_2dba_3{\cdot}CHCl_3$ (2 mol %), PPh_3 (8 mol %), $^iPr_2NEt$.

carbonylation of other allylic substrates such as acetate, carbonate, bromide sulfone, and phenyl ether did not work well.

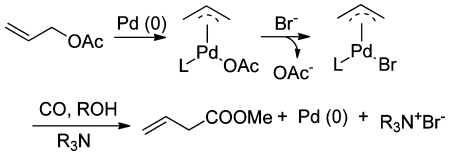
Alper's group reported the synthesis of bicyclic β-lactams from the carbonylative coupling and cyclization reaction of 2-aryl-1,3-thiazines with allyl phosphates.[24] Combining 5,6-dihydro-5,5-dimethyl-2-phenyl-4*H*-1,3-thiazine with triallyl phosphate in the presence of palladium and CO, 61% of the bicycle lactam was produced (Scheme 14).

Scheme 14. Synthesis of Bicyclic β-Lactams



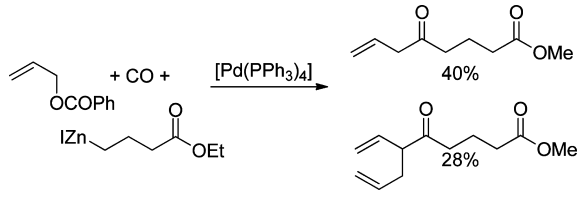
2.4. Allyl Acetates. In 1988, Murahashi and co-workers reported the palladium-catalyzed carbonylation of allyl acetates to produce β,γ-unsaturated esters in moderate to very good yields.[21] Bromide ion was needed probably because of the ligand exchange of allylpalladium acetate with bromide ion to form allylpalladium bromide (Scheme 15).

Scheme 15. Palladium-Catalyzed Carbonylation of Allyl Acetates To Produce β,γ-Unsaturated Esters



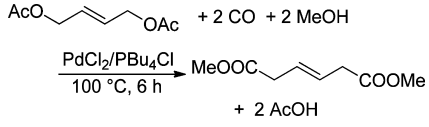
Tamaru reported in 1992 the palladium-catalyzed carbonylation of allyl benzoate with organozinc compound and gave the corresponding substituted ketones.[25] The reaction proceeded smoothly under only 1 bar carbon monoxide and temperature from 0−40 °C. Besides, the use of an aprotic solvent like hexamethylphosphoric triamide (HMPA) or *N*,*N*-dimethylacetamide (DMA) was crucial for the success of this transformation (Scheme 16).

Scheme 16. Palladium-Catalyzed Carbonylation of Allyl Benzoate with Carbon Monoxide and Organozinc Compound for the Synthesis of Substituted Ketones



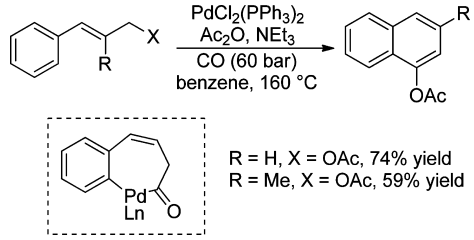
Chan[26] and Kalck[27] found that the addition of tetrabutylphosphonium chloride to $PdCl_2$ could generate efficient catalysts for the dicarbonylation of 1,4-diacetoxy-but-2-ene. During the heating time butadiene was found in the gas phase but was identified as a side-product other than intermediate through control experiments using butadiene as substrate (Scheme 17).

Scheme 17. Palldium-Catalyed Dicarbonylation of 1,4-Diacetoxy-but-2-ene



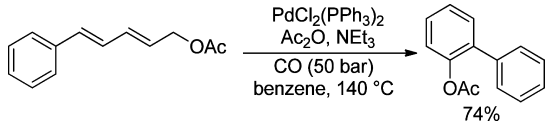
Application of carbonylation reaction with allyl acetates for the synthesis of 1-naphthol derivatives was reported by Hidai and co-workers.[28] The cinnamyl derivative oxidation addition to a palladium(0) species followed by CO insertion and *ortho*-palladation was a possible reaction pathway for this transformation (Scheme 18).

Scheme 18. Palladium-Catalyzed Synthesis of 1-Naphthol Derivatives



They also extend this method to the synthesis of phenyl acetate[29] by cyclocarbonylation of 2,4-pentadienyl acetates in the presence of NEt_3, Ac_2O, and a catalytic amount of $PdCl_2(PPh_3)_2$ at 120−140 °C under 50 bar of CO (Scheme 19).

Scheme 19. Palladium-Catalyzed Synthesis of Phenyl Acetate



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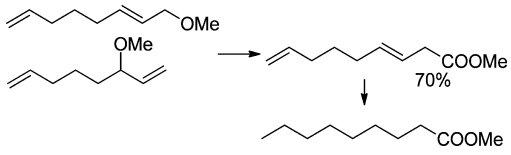
2.5. Allyl Ether. By isolating the isomers from their telomerization reaction of 1,3-butadiene with methanol, the carbonylation of allylic ethers to produce saturated esters was reported by Neibecker and co-workers.[30] Linear esters from C_8 and C_{16} allylic ether were obtained in 70% and 50% yields, respectively. Simple hydrogenation over Adams platinum could produce the corresponding saturated esters in quantitative yield (Scheme 20). They also found that the addition of HCl

Scheme 20. Palladium-Catalyzed Synthesis of Methyl Pelargonate

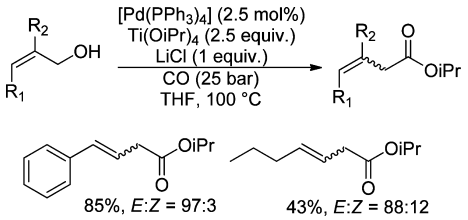


strongly improves the reaction yield but at the expense of product selectivities. Besides, activity and selectivity could be improved simultaneously upon addition of tetrabutylammonium tetrafluoroborate, which indicated that the reaction should proceed via a cationic (η^3-octadienyl) palladium complex.[31]

2.6. Allyl Alcohols. An ideal way to streamline carbonylation of allylic compounds from an economic and environmental point of view is the direct use of allylic alcohols as substrates. Advantageously, the whole synthetic route can be simplified by using allyl alcohols as substrates as the tedious preactivation process can be avoided (most of the above-mentioned substrates are obtained from the corresponding allyl alcohols).

Carbonylation of allylic alcohol was first studied by Alper using nickel catalyst already in 1985 and then with palladium catalyst[32,33] but was studied less until 1992; Miura and co-workers found that the addition of Ti(O*i*Pr)$_4$ and LiCl could accelerate this transformation.[34a] Allyl alcohols might react with Ti(O*i*Pr)$_4$ to afford allyl titanate and react with palladium(0) species to give the π-allylpalladium complex (Scheme 21). In

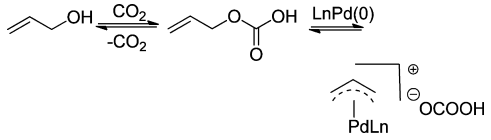
Scheme 21. Carbonylation of Allylic Alcohol in the Presence of Ti(O*i*Pr)$_4$.



1992, Gabriele and co-workers reported the carbonylation of allyl alcohols by using PdI_2 as the catalyst.[34b,c] In the presence of PdI_2, using DMAc as solvent, MeOH as nucleophile under 50 bar of CO at 80 °C, the corresponding esters were produced in good yields with excellent selectivity. In this procedure, as the authors proposed, the in situ generation of allylic iodides from allyl alcohols and HI was the first step.

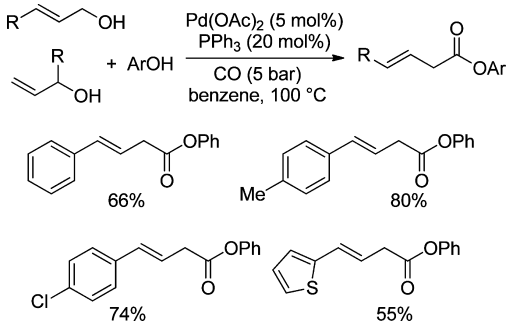
In 1996 Yamamoto's group[35] reported the direct carbonylation of allylic alcohol to unsaturated carboxylic acid using carbon monoxide; interestingly the reaction was accelerated in the presence of carbon dioxide. This effect might be due to a hydrogen carbonate ion formed in the presence of carbon dioxide (Scheme 22).

Scheme 22. Effect of Carbon Dioxide To Form Hydrogencarbonate Ion



Miura et al. reported the palladium-catalyzed carbonylation of allyl alcohols in the presence of phenols as the nucleophiles.[36] In general, good yields were obtained except only 24% yield was obtained with aliphatic alcohol. Besides, the lower yield with aliphatic allylic alcohol might rise from the easily β-H elimination of π-allyl palladium species (Scheme 23).

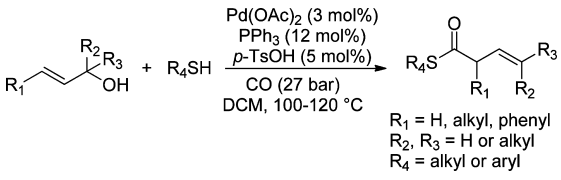
Scheme 23. Palladium-Catalyzed Carbonylation of Allyl Alcohols with Phenols



In 1998, Alper and co-workers reported the palladium-catalyzed thiocarbonylation of allylic alcohol with thiols and carbon monoxide.[37] In this reaction the triphenyl phosphine and acid were crucial for the high yield. First, they found that monodentate phosphine was more active than bidentate phosphine ligand. Then the effect of acids was studied. In the absence of acid additive, there was only 8% yield. The reaction occurs highly regioselectively at the least hindered allylic terminal carbon of the substrates. The established condition was tested with a series acyclic alcohols; by using aryl and aliphatic thiols as the coupling partners the final products were produced in 56−93% yields. Higher temperature and longer reaction time (3−7 days) allowed the cyclic allylic alcohol to afford the thioesters in good yields (Scheme 24).

The first heterogeneous palladium catalyst-catalyzed carbonylation of allylic alcohol was reported by Alper.[38] Using Pd-clay (montmorillonite-bipyridinylpalladium[II]) as catalyst, direct synthesis of β,γ-unsaturated acid from allylic alcohol and carbon monoxide in the presence of HCl was achieved. Indeed, under

Scheme 24. Palladium-Catalyzed Thiocarbonylation of Allyl Alcohol



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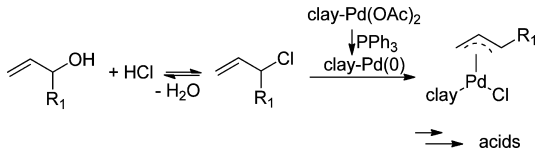
the otherwise same conditions, homogeneous $Pd(OAc)_2$ provides much worse results because of the formation of palladium black. Besides, the Pd-clay could be reused four times without significant losing of its activity. The addition of HCl was supposed for the in situ formation of allyl chloride which after oxidative addition and subsequently carbon monoxide insertion to give the final products (Scheme 25).

Scheme 25. Palladium Clay-Catalyzed Carbonylation of Allylic Alcohol



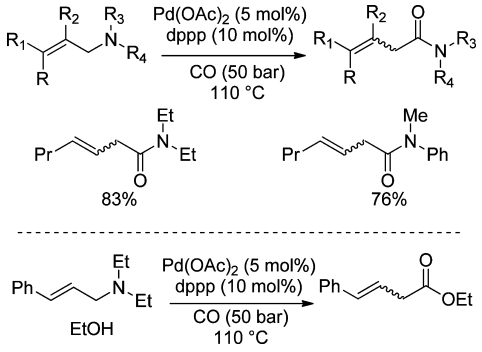
In 2013 Beller and co-workers applied Xantphos and *n*BuPAd$_2$ ligand in the palladium-catalyzed alkoxycarbonylation of allylic alcohols.[39] Not only phenols but also aliphatic alcohols could be used as coupling partners; the corresponding products were produced in good to excellent yields. A domino reaction mechanism was proposed based on the fact that ether was formed first during the reaction process and then carbonylation of allylic ether took place (Scheme 26).

2.7. Allyl Amine. There is only one example on carbonylation of allylic amines in existence until nowadays and amides were produced.[40] Combination of $Pd(OAc)_2$ and 1,3-bis(diphenylphosphino)propane (dppp) (1:2) allowed the conversion of a series of allylic amines into amides in good yields (Scheme 27). Besides, when the reaction was performed in ethanol, the corresponding ester was produced in 77% yield.

3. BENZYLIC COMPOUNDS

Considering the electronical similarity of allylic compounds and benzylic compounds, there were several works using benzylic

Scheme 27. Carbonylation of Allylic Amines To Produce Amides and Esters



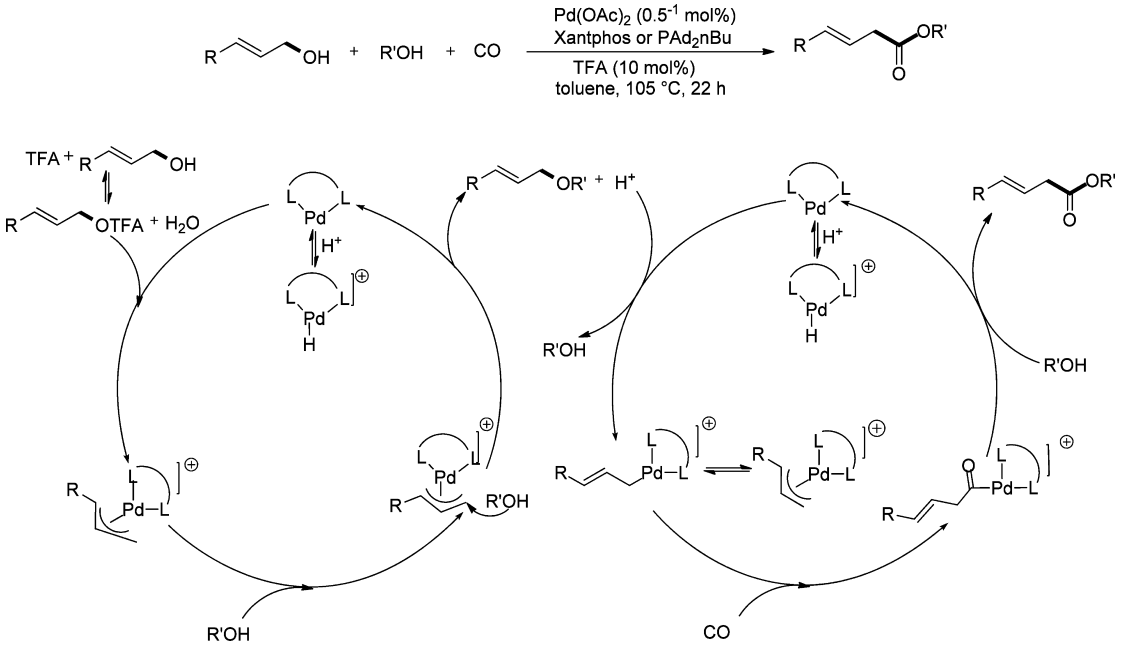
compounds as starting materials in the carbonylation reactions to produce phenylacetic acids and its derivatives.

3.1. Benzyl Halides. In 1974, Heck and co-workers[41] showed one example of a palladium-triphenylphosphine complex catalyzed alkoxycarbonylation reaction of benzyl chloride with carbon monoxide and butanol in the presence of tertiary amine as base. Soon afterward, Hidai[42] reported the methoxycarbonylation of benzyl bromide using palladium complexes: $Pd(CO)(PPh_3)_3$, $Pd_3(CO)_3(PPh_3)_4$, $Pd_3(CO)_3(PPh_3)_3$, and $PdCl_2(PPh_3)_2$.

Normally, more than one equivalent of base was needed to absorb the HX produced in the palladium-catalyzed carbonylations of benzyl halides. Interestingly, there were also some base free systems reported. For example Fuchikami and co-workers found that zeolites such as molecular sieves could serve as an effective sponge of hydrogen halides.[43]

Traditionally, phenylacetic acids were produced from benzyl chloride and cyanide exchange pathway (path a, Scheme 28a). Cassar's group[44] developed a two phase system for the palladium-catalyzed carbonylation of benzyl halides to the corresponding acids. By adding benzyl chloride and PPh_3 slowly into the mixture of aqueous NaOH (30%), [Pd-

Scheme 26. Novel Domino C−O Coupling/Carbonylation Reaction Pathway



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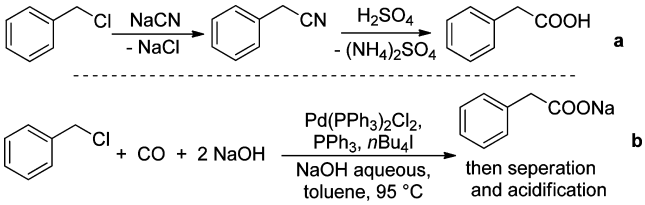
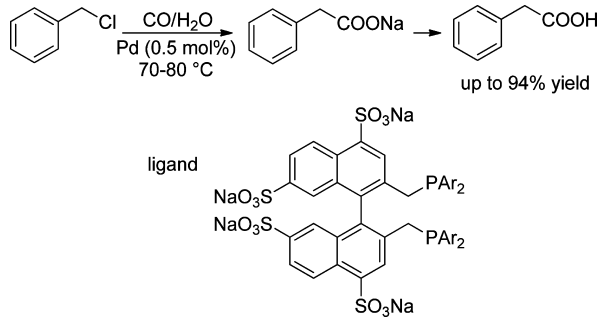
Scheme 28. Two Phase System: Palladium-Catalyzed Carbonylation of Benzyl Chloride



$(PPh_3)_2Cl_2$], and nBu_4I, phenylacetic acid was produced in 83% yield under 5 bar of carbon monoxide at 95 °C. Notably, the organic solution could be recycled many times without obvious loss of catalytic activity. Besides, if *p*-dibromobenzene was used as substrate, a monocarbonylation product was obtained because of the transfer of the *p*-bromobenzoic acid from the organic phase to the aqueous phases (path b, Scheme 28b).

In contrast with Cassar's system (the palladium catalyst was dissolved in the organic phase) Kiji and co-workers[45] reported the NaOH/heptane two-phase system using sulfonated phosphine as ligand which allowed the palladium complex to dissolve in the aqueous phase. This method was further developed by Kohlpaintner and Beller.[46] Using $Pd(OAc)_2$ or $PdCl_2$ and a sulfonated phosphine ligand, carbonylation of benzyl chlorides at atmospheric carbon monoxide pressure produced the corresponding phenylacetic acids in 80−94% yields. Products were obtained from the aqueous phase via separation and extraction with organic solvent. Finally, acidification of the salt generates its free acid. Turnover numbers (TON) greater than 1500 and turnover frequencies (TOF) of 135 h^{-1} were reached (Scheme 29).

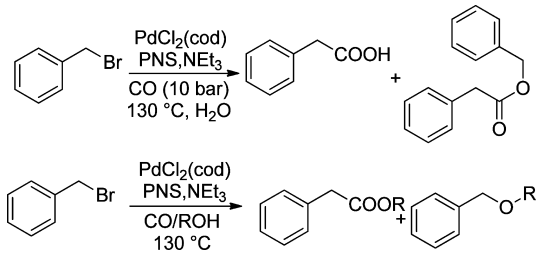
Scheme 29. Palladium-Catalyzed Carbonylation of Benzyl Chlorides To Produce Phenylacetic Acids



A catalytic system containing $PdCl_2$(cod) (cod = 1,5-cyclooctadiene) and a water-soluble phosphine PNS (PNS = $Ph_2PCH_2CH_2C(O)NHC(CH_3)_2CH_2SO_3Li$) in water/toluene solution for the carbonylation of benzyl bromide to produce benzeneacetic acid was reported in 2000 by Ziółkowski and co-workers.[47] The corresponding esters were obtained from alcohols and water mixture solvent. For the synthesis of methyl 2-phenylacetate a TOF of 300 h^{-1} was achieved. The direct reaction of benzyl bromide with acid was observed to be a side-reaction (Scheme 30).

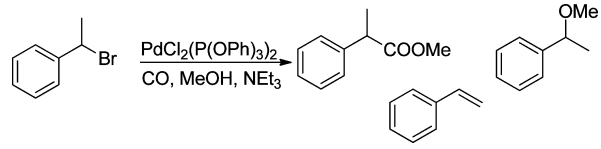
In 1989, Adapa and Prasad reported the carbonylation of benzyl chloride to produce *tert*-butyl phenylacetate under mild conditions.[48] The carbonylation of 1-bromoethylbenzene[47b] was also studied, unlike the benzyl bromide the selectivity to the ester was lower. Apart from the ether, some amount of styrene (10−25%) could be formed as a side-product during

Scheme 30. Carbonlylation of Benzyl Bromide to Benzeneacetic Acid and Esters



the reaction. By adding an excess amount of ligand the yield of the ester could be improved to 70% (Scheme 31).

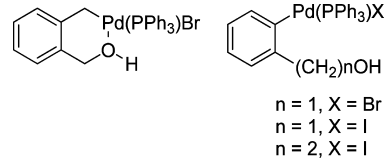
Scheme 31. Carbonylation of 1-Bromoethylbenzene



In 2001, Castanet reported a milder palladium-catalyzed methoxycarbonylation of benzyl chloride.[49] The key to success was the use of magnesium to form methoxide ions and add carbon monoxide after pretreatment (heating the reaction medium in the absence of carbon monoxide) to avoid the formation of palladium carbonyl species which is said to be inactive for methoxycarbonylation reaction. Thus, a low CO pressure (30 °C, 3 bar) and a moderate stirring rate were needed to avoid the deactivation of catalyst.

Organopalladium complexes derived from 2-(bromomethyl) benzenemethanol and 2-bromo- and iodobenzenemethanols[50] (Scheme 32) were equally effective catalysts for the reaction of

Scheme 32. Active Palladium Complexes for the Carbonylation of Benzyl Halides



carbon monoxide and benzyl halides to produce arylacetic acids and esters. Compared to [$PdCl_2(PPh_3)_2$] these catalysts generally gave higher yields (up to 99%) and allowed the reaction to take place at lower reaction temperature.

Apart from the synthesis of acids and esters, ketones and amides from benzyl halide via carbonylation with other nucleophiles were reported as well. Applying commercially available palladium acetate/PCy_3 in the presence of potassium phosphate, Beller's group reported the carbonylative coupling of benzyl chlorides with aryl boronic acids to produce 1,2-diarylethanone.[51] Notably, water could be used as solvent (Scheme 33). Later on, they extended the nucleophiles to potassium aryltrifluoroborates[52] in order to reduce the unwanted noncarbonylative coupling side product.

The direct synthesis of primary benzyl amides using palladium-catalyzed aminocarbonylation of benzyl chlorides and ammonia was also reported.[53] In this reaction, ammonia

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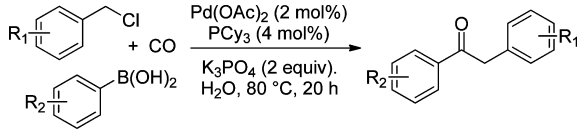
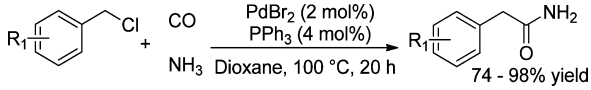
Scheme 33. Carbonylative Coupling of Benzyl Chlorides with Aryl Boronic Acids in Water



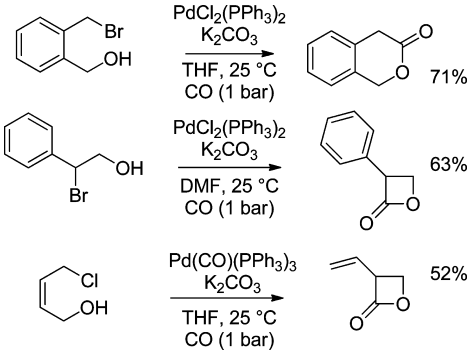
was used not only as the amination reagent but also as base (Scheme 34).

Scheme 34. Aminocarbonylation of Benzyl Chlorides and Ammonia



In 1980, Stille and Cowell reported the intermolecular alkoxycarbonylation of haloalcohols. Lactones were produced in good yields (52−71%) (Scheme 35).[54]

Scheme 35. Palladium-Catalyzed Carbonylative Synthesis of Lactones



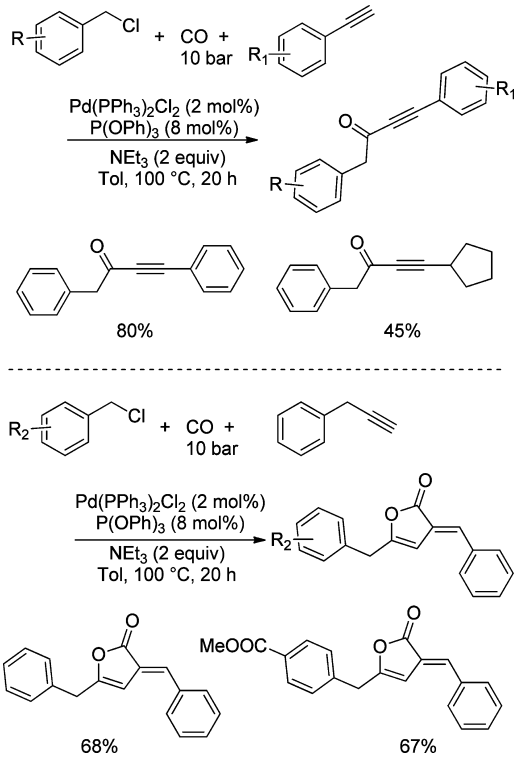
Wu et al. successfully applied benzyl chlorides in the palladium-catalyzed carbonylation reaction with terminal alkynes.[55] Not only aromatic acetylenes but also aliphatic alkynes worked well in this reaction. Interestingly, when benzyl acetylene was used as a coupling partner, furanones was obtained in moderate yields (Scheme 36). The key to their success was the use of electron-poor phosphite ligand.

Based on the work of allyl halides carbonylation and [2 + 2] cycloaddition with imines,[56] Troisi and co-workers reported in 2009 a palladium-catalyzed stereoselective synthesis of 3,4-diaryl β-lactams from benzyl halides and imines (Scheme 37).[57] Benzyl bromides were found to react faster than benzyl chlorides but delivered similar yields of β-lactams.

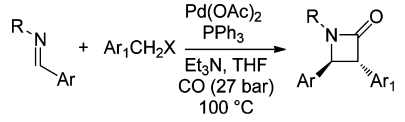
Troisi et al. found that in the case which gave lower yields of β-lactams, a significant amount of the corresponding non-cyclized amides were detected. They explained this by the decomposition of the imine to amine, which will further react with the palladium acyl intermediate to produce the amides. Based on this finding, they developed a general palladium-catalyzed amide synthesis from benzyl halides and amines (Scheme 38).[17]

A general palladium-catalyzed carbonylative synthesis of chromenones from salicylic aldehydes and benzyl chlorides was reported by Wu, Beller, and co-workers in 2013.[58] Various

Scheme 36. Carbonylative Coupling of Benzyl Chlorides with Terminal Alkynes

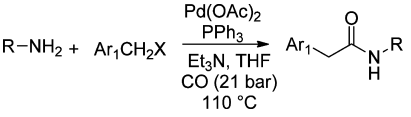


Scheme 37. Synthesis of 3,4-Diaryl β-Lactams from Benzyl Halides and Imines



R = Ph, Ar = Ph; Ar_1 = Ph, X = Br 82% yield *cis:trans* = 4:96
R = Ph, Ar = Ph; Ar_1 = Ph, X = Cl 84% yield *cis:trans* = 8:92

Scheme 38. Palladium-Catalyzed Amides Synthesis from Benzyl Halides and Amines

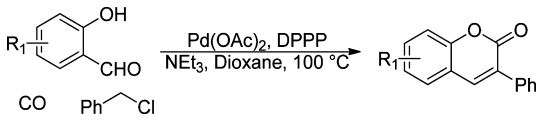


Ar = Ph, X = Br; R = Ph 70% yield
Ar = Ph, X = Cl; R = Ph 81% yield

coumarins were isolated in good to excellent yields (30−95%) (Scheme 39).

Apart from methoxycarbonylation of benzyl chloride using carbon monoxide and methanol, the use of CO surrogates, like methyl formate, was also reported by Castanet and co-workers.[59a] They found that the decarbonylation of methyl formate could be induced by $Mg(OMe)_2$. They also claimed

Scheme 39. Carbonylative Synthesis of Chromenones from Salicylic Aldehydes and Benzyl Chlorides



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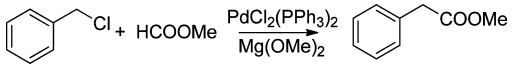
that the addition of extra carbon monoxide actually inhibits the methoxycarbonylation (Scheme 40). Recently, the group of

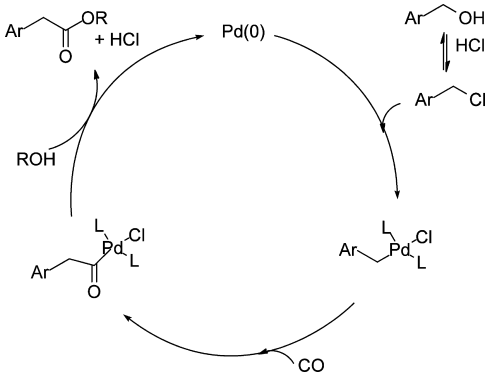
Scheme 40. Methoxycarbonylation of Benzyl Chloride Using Methyl Formate



Skrydstrup developed a nice two-chamber technology for various types of carbonylation reactions. In their substrates testing, benzyl chloride as a specific example was tested. Phenylacetic acid and β-keto ester were produced in good yields after having reacted with HCO_2K and monoester potassium malonates.[59b,c]

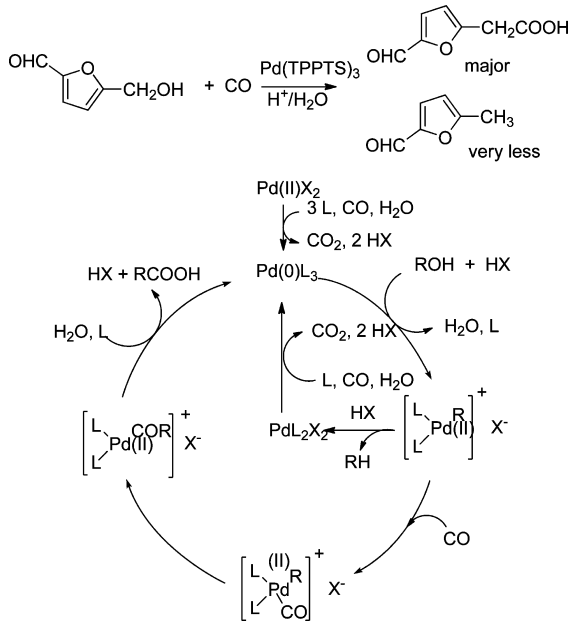
3.2. Benzyl Alcohols. Cavinato and Toniolo reported the palladium-catalyzed carbonylation of benzyl alcohols to phenylacetic acid esters in 1993.[60] Under their conditions, only *para*-hydroxyl substituted benzyl alcohol worked well. Use of $PdY_2(PPh_3)_2$-PPh_3 gave the same results as PdY_2 with equivalent amounts of phosphine (Y = Cl^-, Br^-, I^-, CH_3COO^-). When these precursors were employed in combination with base, catalysis did not occur in an appreciable extent. On the contrary, when HCl was added in a certain amount, slightly higher yields were obtained. These results suggested that the starting benzyl alcohol reacts with HCl to yield the corresponding benzyl chloride and then initiated the catalytic cycle (Scheme 41).

Scheme 41. Palladium-Catalyzed Alkoxycarbonylation of Benzyl Alcohol Derivatives



Sheldon and co-workers reported their detailed studies on the carbonylation of 5-hydroxymethylfurfural (HMF) and benzyl alcohol[61,62] using palladium-trisulfonated triphenylphosphine complexes [$Pd(TPPTS)_3$] under aqueous phase. $Pd(TPPTS)_3$ was easily prepared via complexation of $PdCl_2$ with an aqueous TPPTS solution and reduction with carbon monoxide. The reaction proceeded under very milder conditions (70 °C, 5 bar) producing 5-formylfuran-2-acetic acid (FFA) as the sole carbonylation product. The preferable P/Pd ratio was 6. Besides, the use of weakly or noncoordinating anions such as CF_3COOH and H_3PO_4 favored the carbonylation reaction. Similarly, phenylacetic acid was obtained from benzyl alcohol (Scheme 42). Oxidative addition (S_N1 mechanism) of RX to the palladium forms the cationic alkylpalladium intermediate which allowed the coordination and insertion of CO to the Pd−C bond, nucleophilic attack of water

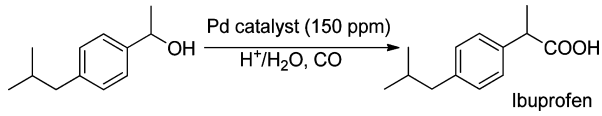
Scheme 42. Palladium-Catalyzed Carbonylation of HMF



to the acylpalladium complex, and elimination to produce the final product (Scheme 42).

Later on, the carbonylation of 1-(4-isobutylphenyl) ethanol to the anti-inflammatory drug ibuprofen was also achieved using water-soluble palladium-phosphine complexes in a two-phase system. Under the optimized conditions, ibuprofen was obtained in 82% yield (Scheme 43).[63,64]

Scheme 43. Direct Synthesis of Ibuprofen from Palladium-Catalyzed Carbonylation Reactions



4. α-HALIDE KETONES

In 1975, one example on the methoxycarbonylation of α-bromoacetophenone using $PdCl_2(PPh_3)_2$ as the catalyst and 1,8-bis(dimethylamino)naphthalene as the base was reported by Stille's group.[65] Their[65] and Adapa's[48] results on the carbonylation of α-halide ketones received less attention until Cavinato[3a] and Beletskaya[66] reported the palladium-catalyzed carbonylation of 2-chlorocyclohexanone and other halomethylketones. Sauthier reported the use of Xantphos ligand in the alkoxycarbonylation of α-chloro ketones with carbon monoxide to produce β-ketoesters in high yields (up to 98%).[67] The scope of the reaction could extend to a wide range of primary and secondary α-chloro ketones as well as alcohols (Scheme 44).

Tandem transformations are green and powerful synthetic tools as they can reduce the environmental impact as well as costs of multistep synthesis.[68] Based on their established catalytic system for the alkoxycarbonylation reaction, Sauthier et al.[69] reported in 2013 a domino reaction consisting of alkoxycarbonylation of α-chloro ketones and a Michael addition reaction to synthesize α-alkylated β-ketoesters (Scheme 45).

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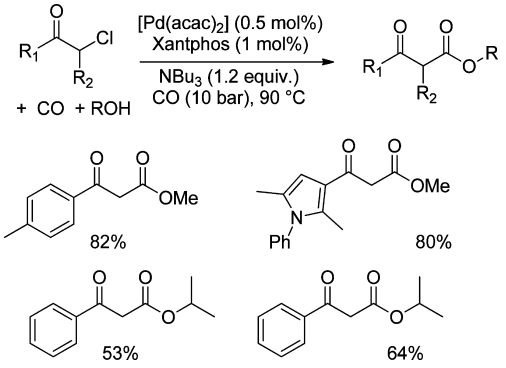
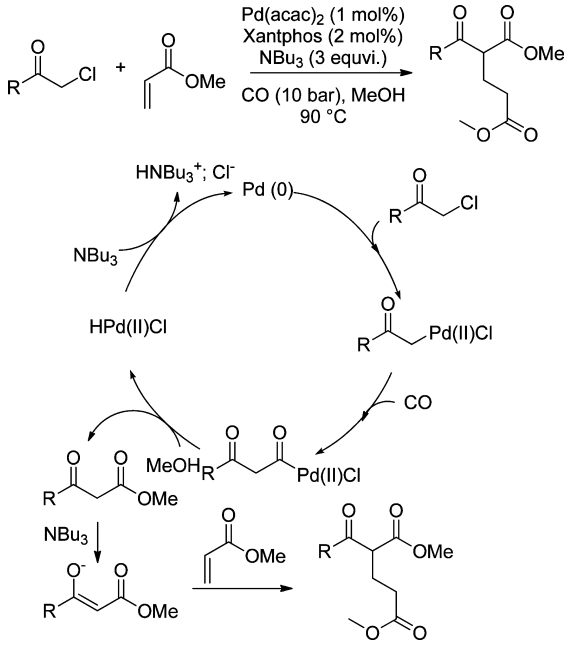
Scheme 44. Efficient Alkoxycarbonylation of α-Chloro Ketones



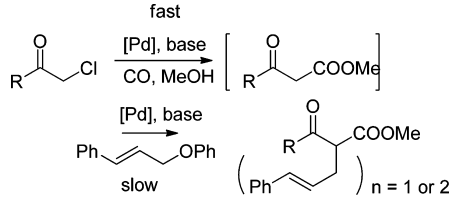
The use of tri-*n*-butylamine was crucial for the deprotonation of the β-ketoesters intermediate.

Scheme 45. Synthesis of α-Alkylated β-Ketoesters by Alkoxycarbonylation/Michael Addition Domino Reaction



Another application of palladium-catalyzed haloketone alkoxycarbonylation in domino reaction sequence was reported by Sauthier and co-workers.[70] The in situ generated β-ketoesters acted as nucleophiles in a subsequent allylation step. In order to reduce side-reactions, less reactive phenoxy was used as a leaving group (Scheme 46).

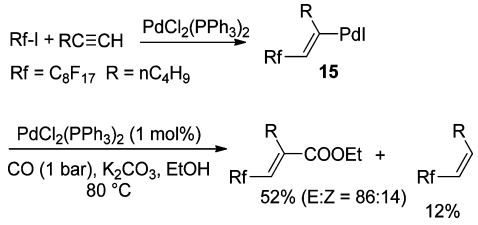
Scheme 46. Straightforward Synthesis of Allylated Keto Esters



5. ALIPHATIC ALKYL HALIDES

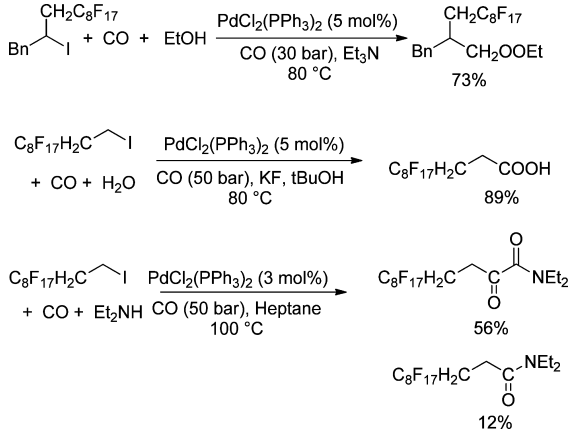
Palladium-catalyzed perfluoroalkyl iodides with terminal alkynes or alkenes in alcohols under carbon monoxide pressure (1−30 bar) were reported by Fuchikami and co-workers.[71] β-Perfluoroalkyl-substituted alkenoates and alkanoates were produced in moderate yields. CO concentration played a role to prevent the reductive elimination of intermediate **15**. The authors assumed that the weak coordination of the fluorine atom to the vacant site of the palladium center might also help to hinder the β-hydride elimination (Scheme 47).

Scheme 47. Palladium-Catalyzed Perfluoroalkyl Iodides Carbonylation with Terminal Alkynes



Based on the fact that β-perfluoroalkyl-substituted alkenyl and alkyl-palladium species easily underwent carbon monoxide insertion, the same author proposed that the oxidative addition complex from perfluoroalkyl iodides might be a possible pathway for the carbon monoxide insertion to produce fluorine containing carboxylic acid derivatives.[72] Indeed when they simply change the base from potassium carbonate to triethylamine, the esterification of 1-perfluorooctyl-2-iodohexane proceeded readily to produce the corresponding ester in 73% yield in the presence of $PdCl_2(PPh_3)_2$ and 30 bar of carbon monoxide (Scheme 48). The acids could also be produced in

Scheme 48. Palladium-Catalyzed Carbonylation of Perfluoroalkyl Iodides



good yields when the reactions were run in the presence of water using *t*BuOH as solvent. Interestingly, using the same system, when amines were introduced in the reactions, double carbonylation[73] to produce the α-keto amides was observed.

In 1991, Fuchikami and co-workers reported the palladium-catalyzed carbonylation of alkyl halides.[74] The easily β-H elimination was the main side reaction and explained the challenge as well. The reaction was performed in a weak basic solvent (*N,N,N′,N′*-tetraalkylurea solution) without additional base (Scheme 49).

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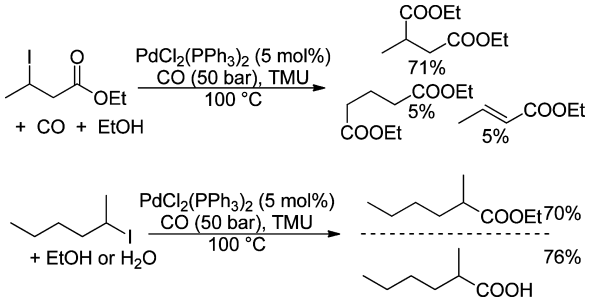
Scheme 49. Palladium-Catalyzed Carbonylation of Alkyl Halides

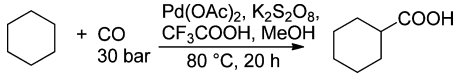


6. C(SP^3)–H

Palladium-catalyzed direct and selective C–H bond functionalization provides a straightforward, economical, and promising synthetic method in organic synthesis.[75] In this respect the palladium-catalyzed C–H bond carbonylation without a prefunctionalized site would be of great interest both in academia and industry.[76] A majority of attention was put on the carbonylation of the C(sp^2)–H bond;[77] on the contrary the palladium-catalyzed C(sp^3)–H carbonylation reactions were rarely reported. The major obstacle is that the presence of CO inhibits the activation of the inert C(sp^3)–H by competitive coordination to Pd.

The first palladium-catalyzed carbonylation of alkane C-(sp^3)–H was reported by Fujiwara and co-workers using $Pd(OAc)_2$, potassium persulfate as oxidant and CF_3COOH as additive. Some amounts of methanol accelerated this reaction (Scheme 50).[78] Though very low yields (TON = 1.95) were

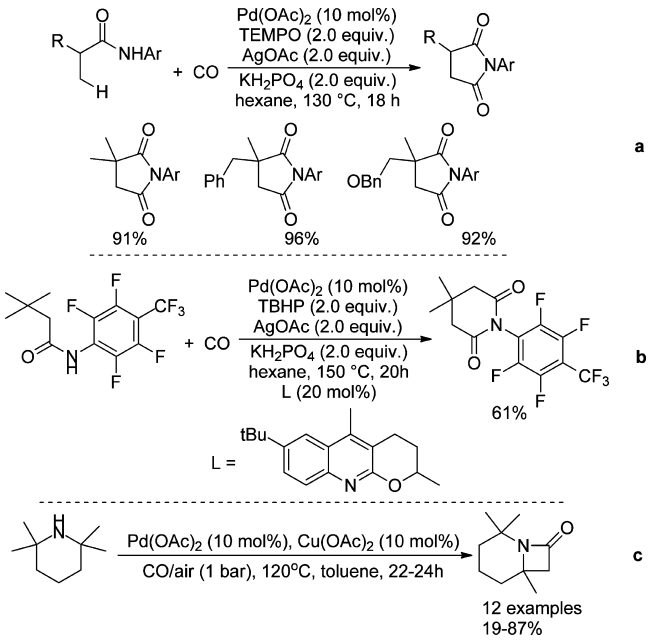
Scheme 50. Palladium-Catalyzed Carbonylation of Alkane



obtained using either cyclohexane or hexane, this work represented a big breakthrough in the palladium-catalyzed C(sp^3)–H carbonylation, as no irradiation was needed for this transformation. Later on, they extended this method to the carbonylation of substituted alkanes, and the reaction occurred regio- and stereoselectively on the carbon with less steric substitution.[79] A higher TON up to 200 was obtained when they reduced the catalyst loading and used $Cu(OAc)_2$ as the cocatalyst.[80]

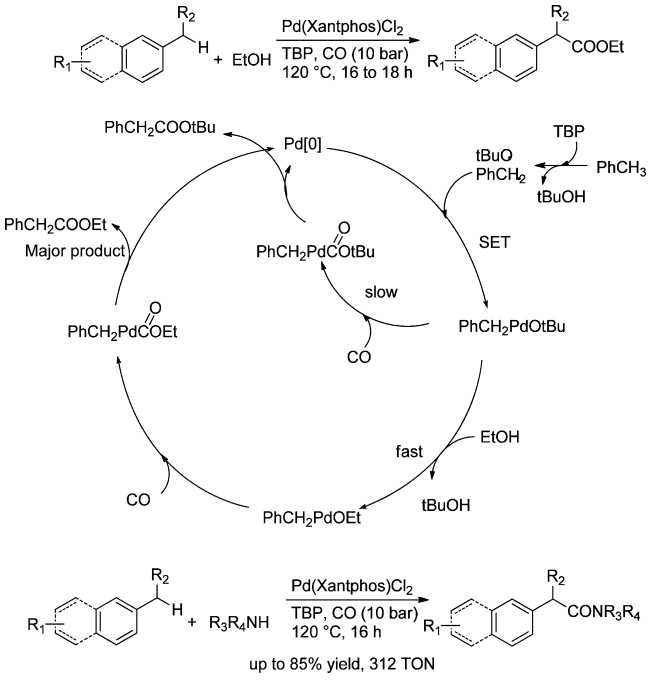
In 2010, Yu and co-workers disclosed the Pd(II) catalyzed β-C(sp^3)–H carbonylation of aliphatic amides to give succinimides which are useful intermediates for many transformations. Apart from AgOAc as the oxidant, the additions of 0.2 equiv of TEMPO highly improve the yield. This method was efficient for substrates containing α-H and cyclopropanes (Scheme 51a).[81a] In 2014, they described a novel palladium-catalyzed olefination of the γ-C(sp^3)–H bond.[81b] In that manuscript, they mentioned one example of intramolecular carbonylative cyclization of γ-C(sp^3)–H with amide (Scheme 51b). In the same year, Gaunt and co-workers reported a palladium-catalyzed C–H bond activation of a methyl group that is adjacent to an unprotected secondary amine into a synthetically versatile nitrogen heterocycle.[81c] Aziridines and β-lactams were selectively produced from the same substrates in the absence or presence of CO (Scheme 51c).

Scheme 51. Pd(II) Catalyzed β-C(sp^3)–H Carbonylation of Methyls



A palladium-catalyzed nondirected benzylic C(sp^3)–H carbonylation to produce substituted 2-phenylacetic acid ester and its derivatives from cheaper starting materials was reported by Huang's group in 2012.[82] A proposed benzylpalladium species generated through the free radical process was illustrated by control experiments with radical scavengers (Scheme 52). The efficiency of this strategy was proved by 21 substrates with moderate to good yields and high TON up to 288. They also found its application in aminocarbonylation reaction to produce amides; good yields (up to 85%) with

Scheme 52. Palladium-Catalyzed Ethoxycarbonylation of the C(sp^3)–H Bond



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TON up to 312 were achieved.[83] Soon after Huang's work, the use of anilines in the amides formation via C(sp^3)−H carbonylation were reported by Dyson.[83b] Notably, cyclohexane also worked and resulted in 43% yield.

7. CONCLUSION AND OUTLOOK

We summarized the developments of palladium-catalyzed carbonylation reactions of C(sp^3)−X compounds. The reactions with allyl compounds, benzyl compounds, α-halide ketones, alkyl halides, and C(sp^3)−H are presented in different sections. A plethora of useful intermediates, final products like β,γ-unsaturated carbonyl compounds, phenylacetic acid, and their derivatives are obtained by the carbonylation reactions with dedicated substrates.

Although remarkable works have been done in this area, significant challenges still exist. For example catalyst efficiency (activity and productivity) is still comparably low; normally 1−5 mol % palladium are needed. The efficiency is much lower compared to the industrial process like palladium-catalyzed methoxycarbonylation of alkenes or reductive carbonylation of aryl halides to aldehydes. Nowadays, several carbon monoxide substitutes (HCOOH, formaldehyde, methyl formate, acid chloride, CO_2, etc.) have been applied in the carbonylation reactions; we believe these methods will be also suitable for the carbonylation of C(sp^3)−X bonds. With regard to sustainability a major challenge will be the development of catalytic carbonylation reactions of alkane by directly C−H activation processes. The advantages of such methods are obvious: cheaper substrates and less waste. Besides, most of the carbonylation reactions use a homogeneous palladium catalyst, while there are only a few reports using heterogeneous palladium catalysts in existence. Obviously, the heterogeneous palladium-catalyzed carbonylations would be interesting as well for bulk chemicals synthesis.

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Notes

The authors declare no competing financial interest.

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