Chapter 6
Carbonylative C–H Activations

Transition metal-catalyzed carbonylation reactions represent an enormous toolbox for CO–X bond formation (X = C, N, O, etc.). While most coupling reactions take place with heteronucleophiles nowadays, carbonylations including C–H activation are attracting more and more attention because the use of stoichiometric amounts of organometallic reagents can be avoided.

The first report on a palladium-catalyzed carbonylative C–H activation was published in 1986 by Kobayashi and Tanaka [1]. They reported that the carbonylation of organic halides with activated methylene compounds in the presence of NEt_3 under 20 bar of CO produces various ketones in good yields (Scheme 6.1). Aryl iodides, bromobenzene and one example of a vinyl bromide were used as starting materials. But relatively high pressure and high pressure are needed, and tri-ethylamine was used both as a base and solvent.

Later on, intramolecular coupling reactions of internal enolates were reported by Negishi and colleagues [2, 3], and 5- or 6-membered rings were synthesized by using the carbonylative C–H activation methodology (Scheme 6.2). In 1998 this group proved that the same reaction can also be catalyzed by $Cl_2Ni(PPh_3)_2$, $Ni(COD)_2$ or Li_2CuCl_4 [4].

In 2002 Larock and Campo reported the palladium-catalyzed cyclocarbonylation of *o*-halobiaryls [5, 6], giving various substituted fluorenones in high yields (Scheme 6.3). The cyclocarbonylation of 4′-substituted 2-iodobiphenyls generates 2-substituted fluorenones, incorporating either electron-donating or electron-withdrawing substituents. Similarly, 3′-substituted 2-iodobiphenyls afforded 3-substituted fluorenones in excellent yields with good regioselectivity. The authors also succeeded in extending the reaction to polycyclic fluorenones, fused isoquinoline, indole, pyrrole, thiophene, benzothiophene, and benzofuran rings.

In 2007 the palladium-catalyzed coupling of aryl or vinyl iodides with ethyl diazoacetate was published by Wang and his team [7]. It was the first example of using α-diazocarbonyl compounds as a coupling partner in a palladium-catalyzed carbonylation reaction (Scheme 6.4).

In 2010 Beller' group developed a general yet efficient methodology for the carbonylative coupling between aryl iodides and heteroarenes [8]. This represented the first carbonylative C–H activation reactions of heteroarenes to form diarylketones.

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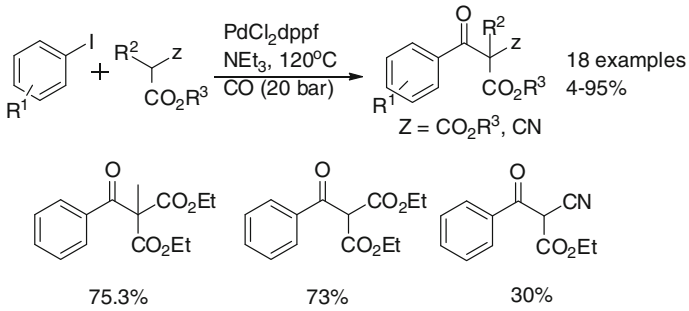
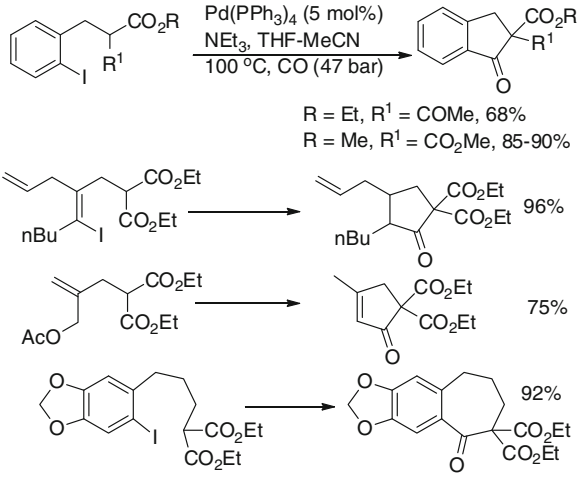


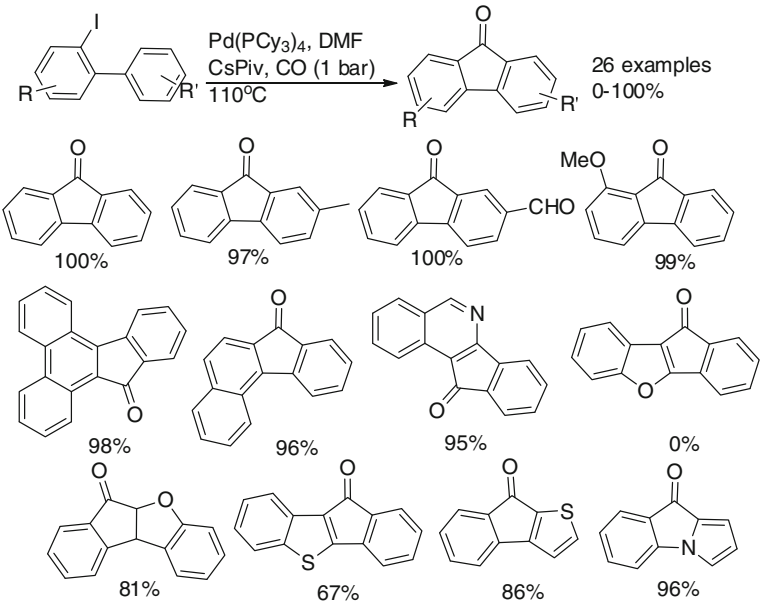
Scheme 6.1 Pd-catalyzed carbonylative coupling with activated methylene compounds

Scheme 6.2 Pd-catalyzed intramolecular carbonlative C–H activations

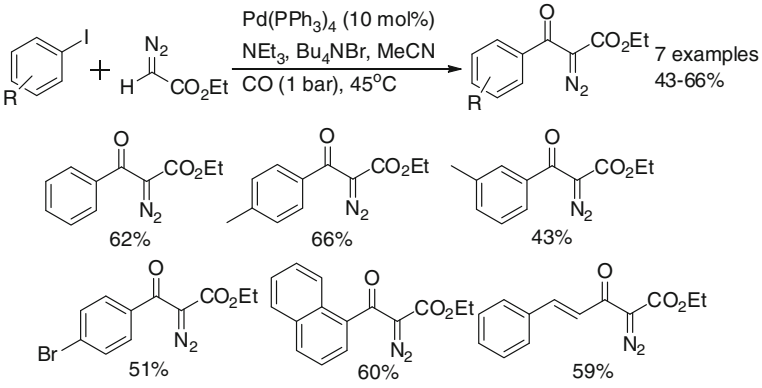


Applying various aryl iodides and different heterocycles, such as oxazoles, thiazoles, and imidazole in the presence of a Pd/Cu system, the corresponding coupling products are obtained in a straightforward manner in moderate to good yields (Scheme 6.5). Compared with established carbonylative cross-coupling reactions for the synthesis of ketones, no additional organometallic reagents are needed, making the protocol as an useful extension of palladium-catalyzed coupling reactions.

Above we mentioned the palladium-catalyzed carbonylative coupling of organohalides with C–H nucleophiles. Compared with their version of carbonylative coupling with organometallic reagents, the pre-activation of C–H bonds was not needed. The other pathway in carbonylative C–H activation is the reaction between two nucleophiles in the presence of an additional oxidant; sometimes these types of reactions are also called oxidative carbonylations. Only the reaction between Ar–H and nucleophiles will be discussed in the following; the other oxidative carbonylation reactions will be summarized in Chap. 8.

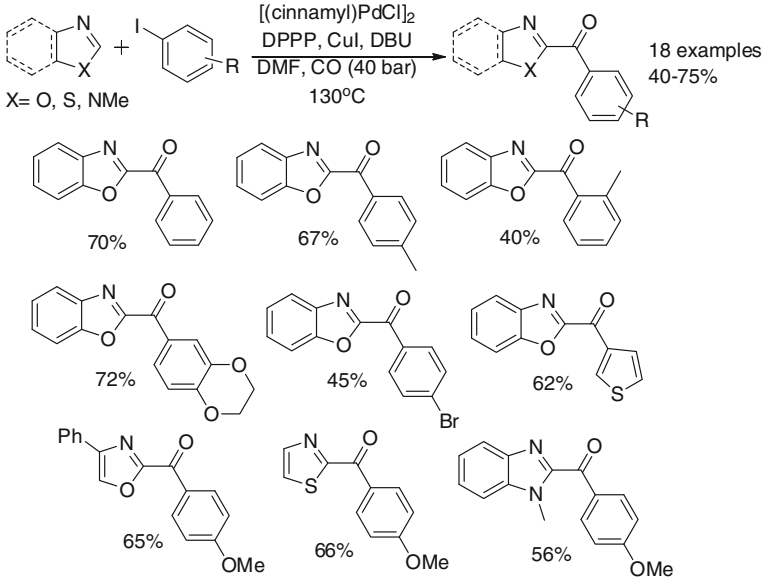


Scheme 6.3 Pd-catalyzed carbonylative synthesis of fluorenones



Scheme 6.4 Pd-catalyzed carbonylative coupling reactions of aryl iodides with α-diazocarbonyl compound

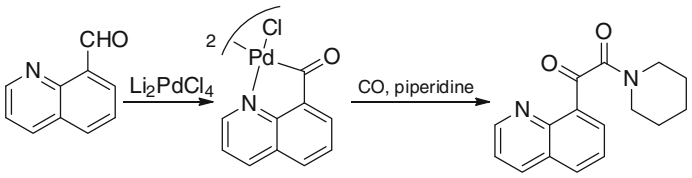
In 1980 Fujiwara and colleagues described for the first time a palladium-mediated oxidative carbonylation of arenes to benzoic acids [9–11]. The direct carboxylations of benzene, toluene, anisole, chlorobenzene, furan, and thiophene were carried out under CO and in the presence of $Pd(OAc)_2$. 2–43 % of the corresponding benzoic acids were formed as the terminal products. Later on, the reaction was performed with a catalytic amount of palladium salts using *tert*-



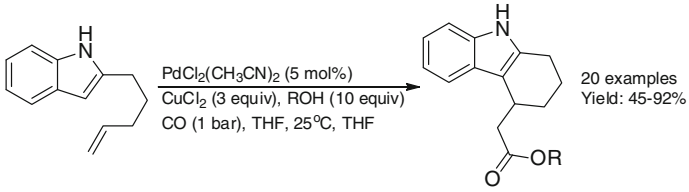
Scheme 6.5 Pd-catalyzed carbonylative coupling of ArI with heteroarenes

BuOOH, or $K_2S_2O_8$ as an additional oxidant. After the original work of Fujiwara, the C–H functionalization of simple arenes was investigated by other groups, too. In this respect, Itahara reported on the palladium-promoted oxidative carbonylation of 1-acylindoles, thiophenes, and 1,3-dimethyluracils to produce the corresponding carboxylic acids under atmospheric pressure of CO in 1982 [12, 13]. Palladium-catalyzed carbonylation of aromatic aldehydes and hydrocarbons to α-keto amides were developed by Yamamoto and his team [14]. Aromatic aldehydes were allowed to react with tertachloropalladate (II) via C–H activation to produce the corresponding aroylpalladium complexes, which afford α-keto amides after subsequent quenching with CO and piperidine in high yields (Scheme 6.6). A similar procedure was also described using 2-*tert*-butyl-4,4-dimethyl-2-oxazoline [15].

Dixneuf's group developed an interesting synthesis of heteroaromatic esters by a palladium-promoted oxidative carbonylation of thiophene, furan, benzofuran,



Scheme 6.6 Palladium-mediated carbonylation of C–H bonds



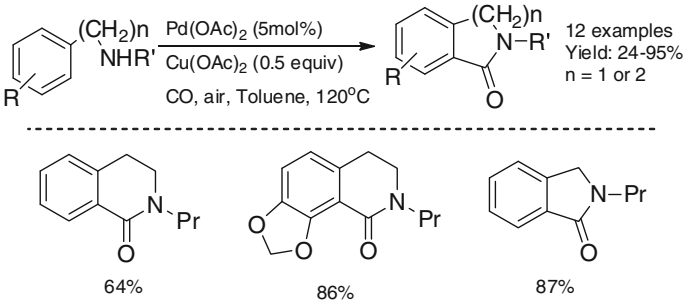
Scheme 6.7 Palladium-catalyzed cyclization/alkoxycarbonylation of alkenyl indoles

and pyrrole in the presence of alcohol [16]. The reaction proceeded at room temperature, but 50 bar of CO was required. The presence of mercury salt and copper(II) salt to reoxidize the Pd(0) species was also necessary. Later on, Ugo and colleagues succeeded in improving this methodology and described the reaction under 1 bar of CO [17]. In 2004, Nozaki and his team studied the hydroxycarbonylation of biphenyls via C–H activation processes. Using formic acid as a carbonyl source to avoid the management of CO gas, the palladium-catalyzed oxidative carbonylation was carried out in trifluoroacetatic acid in the presence of $K_2S_2O_8$ as an oxidant. Moderate yields of carboxylic acids were achieved, but the regioselectivity was problematic [18]. Phosphenium salts as strong electron-withdrawing ligands[19–21] proved to be effective in this catalytic system [22].

Tetrahydrocarbazoles and related compounds constitute heterocycles occurring both in pharmaceuticals and agrochemicals. Hence, it is interesting that Widenhoefer and Liu succeeded with palladium-catalyzed oxidative carbonylations for the synthesis of tetrahydrocarbazoles [23, 24]. Starting from alkenyl indoles in the presence of $PdCl_2(CH_3CN)_2$ (5 mol%) and $CuCl_2$ (3 equiv) under 1 bar of CO in THF, the corresponding products were obtained in good yields with high regioselectivity (Scheme 6.7). A possible reaction pathway has also been given for this cyclization.

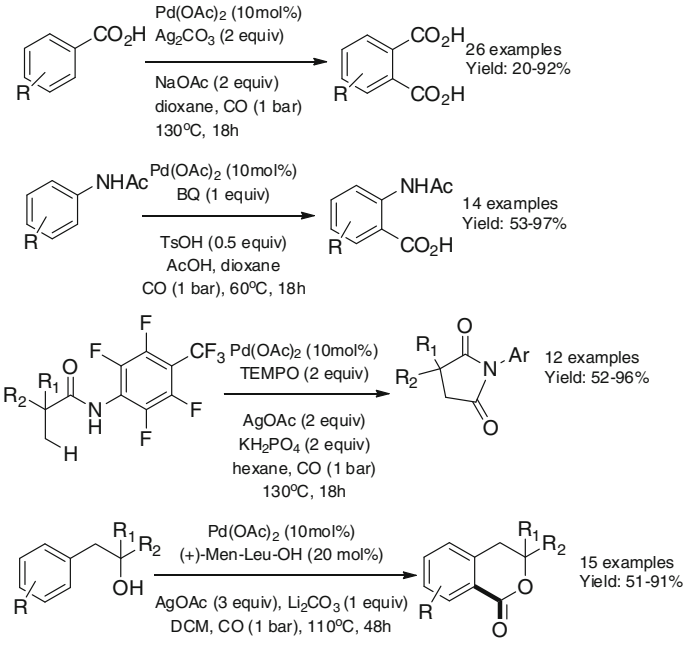
The group working with Orito reported on the synthesis of benzolactams via carbonylative C–H activation [25–27]. The assistance of $Cu(OAc)_2$ and the presence of CO (1 bar) and air were important for this transformation. The direct carbonylation reaction proceeded in a phosphine-free catalytic system with remarkable site selectivity to afford a variety of five- or six-membered benzolactams from secondary *w*-phenylalkylamines (Scheme 6.8). In the case of primary amines, the corresponding ureas were produced. With regard to the mechanism, the ortho-palladation of methyl L-phenylalanate and the depalladation with CO forming tetrahydroisoquinoline were carried out in a step-by-step study by Vicente and his colleagues [28].

In a series of papers, Ishii's group described their developments for the carboxylation of anisoles, biphenyls, and benzenes [29–31]. Applying a combination of $Pd(OAc)_2$ (5 mol%) and HPMoV (molybdovanadophosphates, 2 mol%) under pressure of CO (0.5 bar) and O_2 (0.5 bar), carboxylic acids were formed in AcOH in fairly good yields with fair to good selectivity.

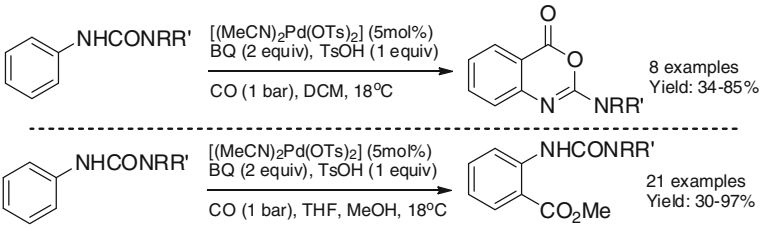


Scheme 6.8 Palladium-catalyzed carbonylative synthesis of benzolactams

Also, Yu and colleagues described several novel methodologies for the palladium-catalyzed oxidative carbonylative C–H activation of arenes. 1,2- and 1,3-dicarboxylic acids have been selectively produced from the corresponding benzoic acids under the assistance of $Pd(OAc)_2$ (10 mol%), Ag_2CO_3 (2 equiv) and NaOAc (2 equiv) in the presence of CO (1 bar) at 130 °C [32]. Anthranilic acids, oxazolinones, and quinazolinones were synthesized from corresponding anilindes by applying BQ as an oxidant and TsOH as an additive [33–35]. Interestingly, they used amino acids as ligands to promote the oxidative carbonylation of phenethyl



Scheme 6.9 Palladium-catalyzed oxidative carbonylation of arenes



Scheme 6.10 Palladium-catalyzed oxidative carbonylation of aniline derivatives

alcohols to 1-isochromanones (Scheme 6.9). Recently, this group also succeeded in applying sulfonamide as a directing group in palladium-catalyzed oxidative carbonylative C–H activations [36].

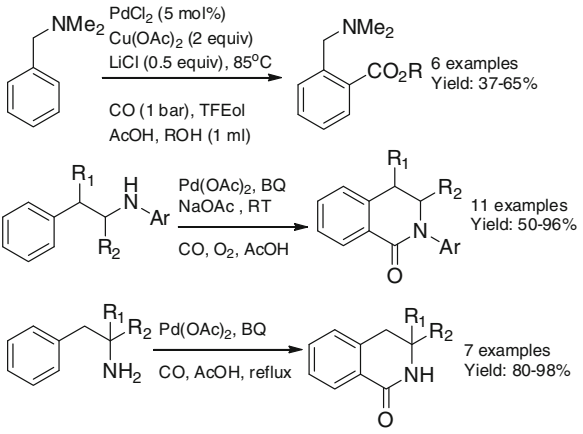
An interesting oxidative carbonylation of aniline derivatives was published in 2009 [37]. The reaction proceeded under 1 bar of CO at room temperature with 5 mol% of $[Pd(OTs)_2(MeCN)_2]$ as the precatalyst. Either cyclic imidates or methyl anthranilates can be easily generated, depending on the reaction conditions. The use of *N*-aryl urea derivatives with a terminal N–H moiety allowed for the generation of quinazolinones (Scheme 6.10).

The oxidative carbonylation of benzotrifluoride to form trifluoromethylbenzoic acids has been described by Bell and Zakzeski [38]. By using a Pd(II) catalyst in combination with a carboxylic acid, ammonium metavanadate, CO, and O_2, trifluoromethylbenzoic acid was achieved in good selectivity. Shi and his colleagues performed LiCl-promoted Pd(II)-catalyzed oxidative carbonylation of *N,N*-dimethylbenzylamines [39]. This reaction is highly regioselective and the product can be further transformed into *ortho*-methyl benzoate under mild conditions.

At the same time, Gaunt's group published a method in which they started from secondary *β*-arylethylamines to obtain dihydro-2-quinolones [40], and Granell's and Garcia's group developed a procedure for the carbonylation of *N*-unprotected arylethylamines (Scheme 6.11) [41].

Finally, oxidative carbonylations of simple ketones, such as hexanone and pentanone, were reported to give diesters [42, 43]. In the presence of $PdCl_2$, $CuCl_2$, CO, and in methanol, various diesters have been produced in good yields from corresponding cyclic ketones.

Zhu and his team developed an unprecedented C–H aminocarbonylation reaction using unprotected aniline NH_2 as a directing group [44]. Various free (NH)-phenanthridinone derivatives were efficiently synthesized in the presence of $Pd(TFA)_2$ as a catalyst and $Cu(TFA)_2$ as a stoichiometric oxidant under an atmospheric pressure of CO starting from *o*-arylanilines (Scheme 6.12). The resulting free (NH)-phenanthridinone skeleton can be readily diversified following known methods, including *N*-alkylation, *N*-arylation, Suzuki coupling of the chloride, or triflate intermediates. Some *ortho*-heteroarene substituted anilines can also be applied in this C–H aminocarbonylation reaction, giving polyheterocycles



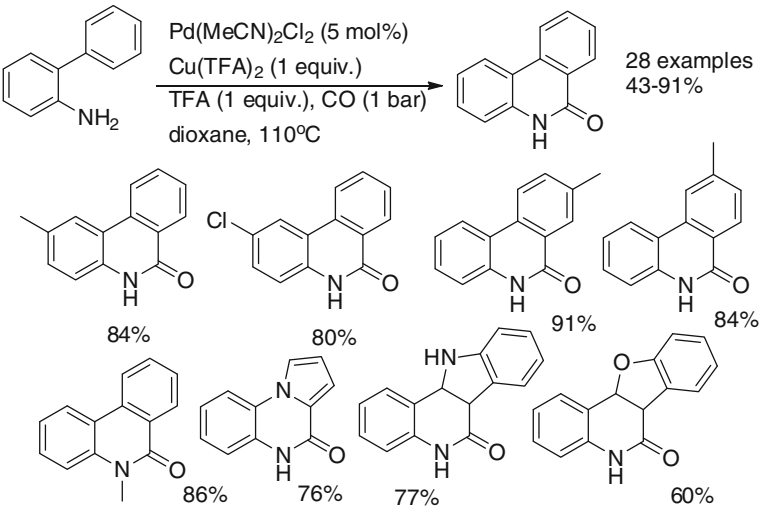
Scheme 6.11 Palladium-catalyzed oxidative carbonylation of anilines

containing a free (NH)-lactam moiety, which exists in many bioactive relevant molecules.

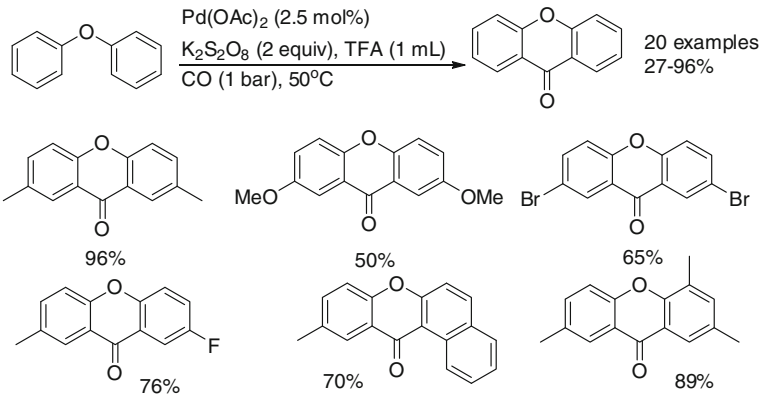
Lei and his associates developed a Pd-catalyzed double C–H functionalization/carbonylation of diaryl ethers to form xanthones [45]. By using a simple catalytic system consisting of $Pd(OAc)_2$, $K_2S_2O_8$, and TFA, a variety of diaryl ethers could be directly carbonylated to xanthones in moderate to good yields (Scheme 6.13). Moreover, various functional groups were tolerated under the optimized conditions. Notably, this transformation provides an effective and practical protocol for the syntheses of bioactive xanthones.

Huang's group succeeded in developing an efficient Pd-catalyzed carbonylation of benzylic C–H bonds with CO through nondirected $C(sp^3)$-H bond activation [46]. This carbonylation process represents a practical and effective methodology for the synthesis of substituted phenylacetic acid esters from simple toluenes. The new strategy for the generation of such a benzylpalladium intermediate should pave the way to some new classes of C–H functionalization reactions, complementary to the classical synthetic methods with organic halides. At the same time, Guan and colleagues developed a novel palladium-catalyzed C–H bond carbonylation of *N*-alkyl anilines for the synthesis of isatoic anhydrides [47]. The mechanism was investigated, and a key intermediate was isolated and characterized. This novel palladium-catalyzed carbonylation reaction tolerates a wide range of functional groups and is a reliable method for the rapid elaboration of readily available *N*-alkyl anilines into a variety of substituted isatoic anhydrides under mild conditions (Scheme 6.14).

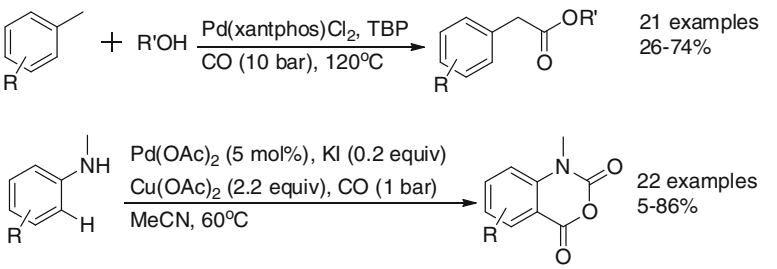
Indoles as an important class of heterocycles were studied in carbonylations as well. In 2011, Lei's team developed an interesting procedure for the carbonylative transformation of indoles to the corresponding esters [48]. High regioselectivity was obtained and an electrophilic palladation mechanism was proposed. More recently, Lei's group developed some novel methodologies for the carbonylation of indoles [49–51]. Amides, α-ketoamides, esters, and alkynones were produced in good yields with I_2 as an oxidant (Scheme 6.15).



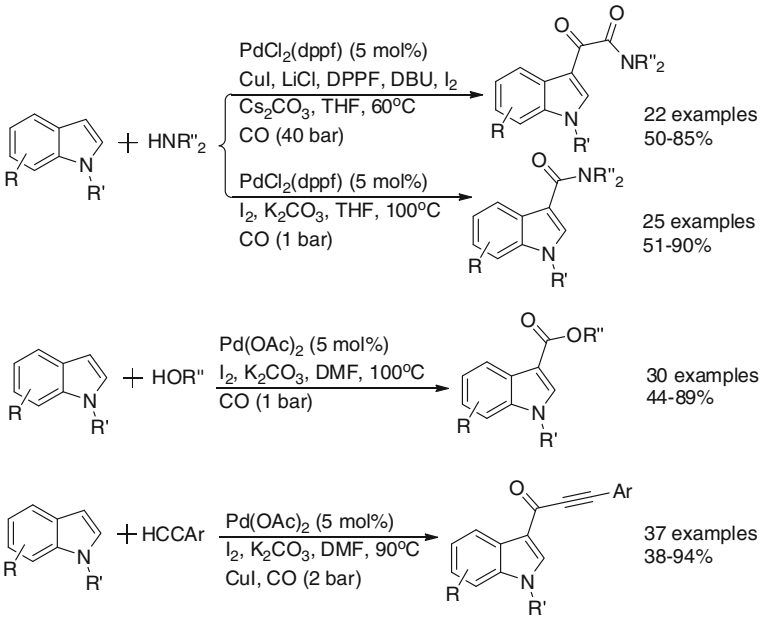
Scheme 6.12 Palladium-catalyzed oxidative carbonylation of *o*-arylanilines



Scheme 6.13 Palladium-catalyzed carbonylation of diaryl ethers



Scheme 6.14 Palladium-catalyzed carbonylative activation of Csp^3-H

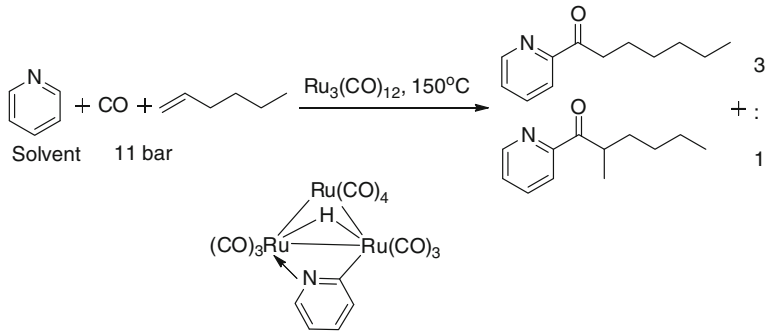


Scheme 6.15 Carbonylative transformation of indoles

In addition to palladium catalysts, ruthenium catalysts were applied in carbonylative C–H activation reactions as well. Moore and colleagues described the first ruthenium-catalyzed carbonylative C–H activation reaction in 1992 [52]. O*rtho*-acylation of pyridine and other nitrogen-containing aromatic compounds can be carried out with olefins and CO, using $Ru_3(CO)_{12}$ as the catalyst (Scheme 6.16). Interestingly, internal olefins, such as *cis*- and *trans*-2-hexene, yield the same linear/branched product ratio as terminal olefins.

Some other transition metal carbonyl compounds were also investigated instead of $Ru_3(CO)_{12}$, such as $Os_3(CO)_{12}$, $Rh_4(CO)_{12}$, $Re_2(CO)_{10}$, but none of them showed any activity in this reaction. The mechanism behind this reaction was most likely the fact that a coordinatively unsaturated metal center of the trinuclear cluster is attacked and coordinated by pyridine, and subsequent *ortho*-metalation gives the key intermediate. Olefin insertion into a linear and branched alkyl species, followed by CO coordination and insertion, produces the acyl species, which reacts further to the acylated product by reductive elimination.

One main issue for Moore's procedure is that the reaction needs a substrate as solvent. In 1996, Murai and his researchers solved this challenge [53, 54] by carrying out the coupling reaction with imidazoles in toluene, under 20 bar of CO, at 160 °C. After 20 h, various substituted imidazoles were acylated under the assistant of 4 mol% of $Ru_3(CO)_{12}$. The reaction proceeded with excellent linear selectivity. Besides imidazoles, 1-methylpyrazoles were also acylated in good



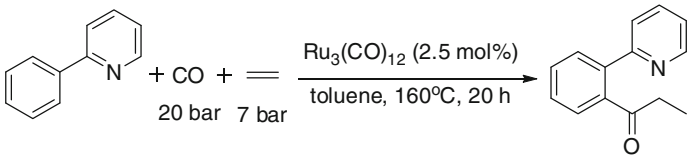
Scheme 6.16 $Ru_3(CO)_{12}$ catalyzed carbonylation of pyridine

yields. Not only aliphatic alkenes, but styrenes were successfully applied as coupling partners as well.

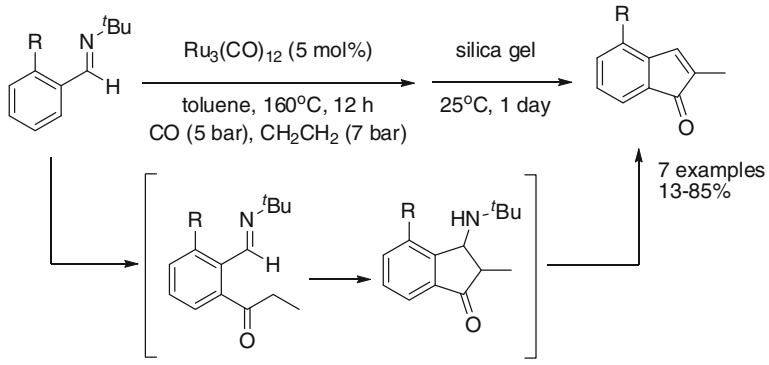
Later, Murai's group described the ruthenium-catalyzed carbonylation of pyridylbenzenes (Scheme 6.17) [55]. Pyridylbenzenes were acylated with ethylene in the presence of a catalytic amount of $Ru_3(CO)_{12}$ in toluene at 160 °C under 20 bar of CO. This reaction was also successful in using naphthyl and thienyl rings. Other effective directing groups for carbonylation at a C–H bond in the benzene ring are six-membered heterocycles, such as 2-pyrimidine and 4-pyrimidine. Besides ethylene, trimethylvinylsilane and *tert*-butylethylene can also be used as coupling partners for this reaction. However, this procedure failed with substrates as 1-hexene, cyclohexene, allyltrimethylsilane, styrene, methyl methacrylate, vinyl acetate, triethoxyvinylsilane, and isopropenyltrimethylsilane.

In 1997 Murai's group developed a two-step procedure for the synthesis of 2-substituted inden-1-ones [56]. The reaction pathway comprised a carbonylation at a C–H bond and subsequent intramolecular aldolcondensation. Aromatic imines were applied as starting materials and coupled with both ethylene and trimethylvinylsilane to yield indenones in moderate to good yields (Scheme 6.18).

$Ru_3(CO)_{12}$-catalyzed carbonylation at an olefinic C–H bond was also reported in 1998 by Murai's group [57]. The propionylation of pyridylolefins at an olefinic C–H bond with CO and ethylene proceeds with a catalytic amount of $Ru_3(CO)_{12}$ in toluene. The carbonylation occurs regioselectively at the γ-position to the pyridine nitrogen and ethylene serves as the only olefin, which can be used successfully.



Scheme 6.17 $Ru_3(CO)_{12}$ catalyzed carbonylation of pyridylbenzene



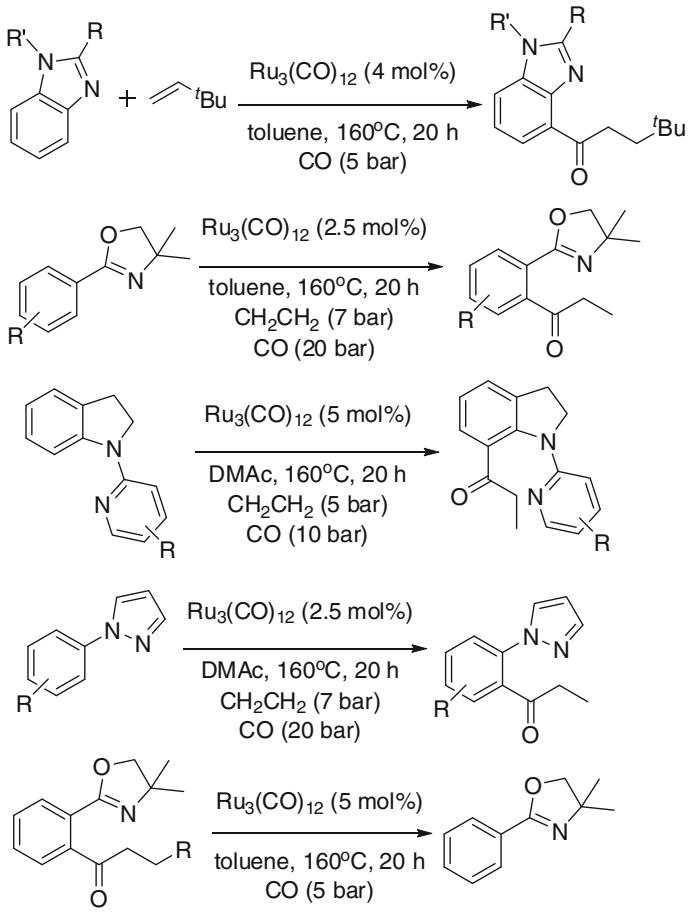
Scheme 6.18 $Ru_3(CO)_{12}$ catalyzed carbonylative synthesis of indenones

Using transition-metal complexes other than $Ru_3(CO)_{12}$, no catalytic activity has been exhibited so far. This reaction can also be extended to *N*-(2-pyridyl)enamines, giving the corresponding ethyl ketones as the coupling products. Here the pyridine ring is separated from an olefin unit by a sp^3-nitrogen atom. Interestingly, this reaction also shows high catalytic activity using $Rh_4(CO)_{12}$. In addition, other olefins, such as propene, 1-hexene, 3,3-dimethyl-1-butene, styrene, cyclopentene, acryl acid methyl ester, ethyl vinyl ether, and trimethylvinylsilane can also be used as a coupling partner.

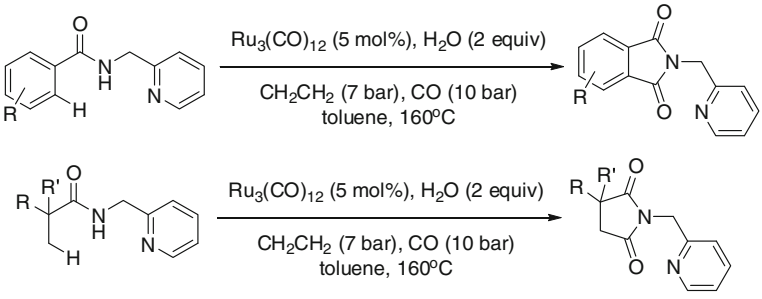
In addition to the above-mentioned reactions, Murai's group developed several other ruthenium-catalyzed carbonylations of arenes with similar reaction conditions (Scheme 6.19). Here, aza-heterocycle [58], 2-phenyloxazolines [59], *N*-pyridylindolines [60], *N*-arylpyrazoles [61, 62], and 2-phenylpyridines [63], were carbonylated into the corresponding products with $Ru_3(CO)_{12}$ or Ru/C as the catalyst. Besides these novel carbonylation reactions, ruthenium-catalyzed decarbonylative cleavage of alkyl phenyl ketones producing phenyl derivatives were also discovered by this group [64].

More recently, Chatani and his researchers developed the ruthenium-catalyzed carbonylation at the *ortho*-C–H bonds of aromatic amides [65] to give phthalimides as their products. Analogously, this reaction can also be transferred to even inactivated $C(sp^3)$-H bonds and yield the corresponding succinimides. (Scheme 6.20) [66] In both cases, the presence of 2-pyridinylmethylamino moiety is necessary for these transformations, because it plays an important role as a *N*,*N*-bidentate ligand to form a dinuclear ruthenium complex with $Ru_3(CO)_{12}$. Interestingly, in the absence of ethylene, no carbonylation product could be detected while the efficiency of the reaction decreased in the absence of water. In the latter case, a long reaction time (5 days) is still needed.

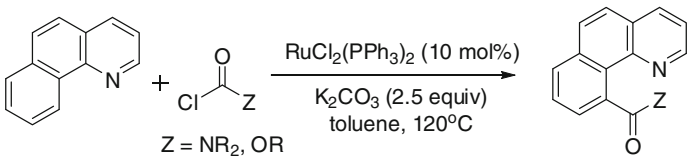
A CO-free acylation of arylpyridines was developed by Kakiuchi and colleagues (Scheme 6.21) [67, 68]. In the presence of a catalytic amount of ruthenium catalyst, arylpyridines were coupled with acyl chlorides, carbamoyl chlorides, and alkyl chloroformates in moderate to good yields. This procedure offers an alternate



Scheme 6.19 Ruthenium-catalyzed carbonylative C–H activations

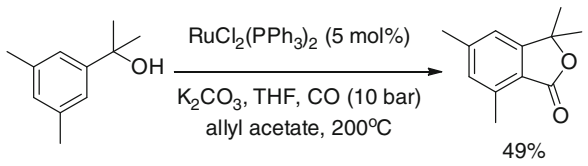


Scheme 6.20 Ruthenium-catalyzed carbonylation of amides



Scheme 6.21 Ruthenium-catalyzed acylation of arenes

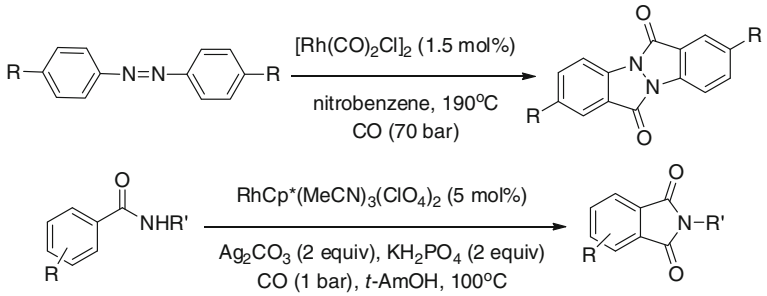
Scheme 6.22 Ruthenium-catalyzed oxidative carbonylation of allylic alcohols



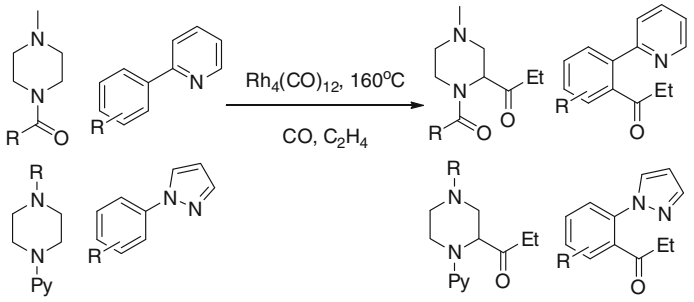
method for the direct alkoxy and amido carbonylation of arenes, even in those cases where the usual Friedel–Crafts methods are difficult.

Lactones are heterocyclic rings that commonly occur in natural compounds, which exhibit potential biological activities. The first ruthenium-catalyzed carbonylative synthesis of 2-furanones was developed by Watanabe and colleagues in 1994 [69]. In the presence of catalytic amounts of ruthenium catalyst, 2-furanones were prepared in moderate to high yields from corresponding allylic alcohols. Since this oxidative cyclocarbonylation reaction releases one equivalent of hydrogen, and a hydrogen acceptor was used. While allyl acetate works well, other acceptors, such as acetone, cyclohexene, and diphenylacetylene were not useful for this transformation. A combination of $Ru_3(CO)_{12}$ and $RuCl_3{\cdot}nH_2O$ with triaryl- or trialkyl-phosphines can also promote this reaction, but a considerable amount of saturated lactones was obtained. No carbonylation was observed by using other transition metals, such as $NiBr_2(PPh_3)_2$, $RhCl(PPh_3)_3$, $PdCl_2(PPh_3)_2$ and $PtCl_2(PPh_3)_2$, demonstrating the superior activity of ruthenium in this reaction. Notably, the same catalytic system was also applied for the oxidative cyclization of 4-penten-1-ols (Scheme 6.22) [70]. The reaction proceeded at 160 °C in the presence of $Ru_3(CO)_{12}$ and PPh_3 under 5 bar of CO.

Additionally, rhodium catalysts were explored in this area as well. Takahashi's group reported a rhodium-catalyzed cyclocarbonylation of azobenzenes in 2004 [71]. With the assistance of this rhodium catalyst, indazolo[2,1-a]indazole-6,12-diones were achieved in good yields using nitrobenzene as a hydrogen acceptor (Scheme 6.23). In contrast, performing the carbonylation of azobenzene via a cobalt catalysis, quinazoline was obtained as the final product. More recently, Rovis's group reported rhodium-catalyzed carbonylative C–H activation of benzamides [72]. This novel strategy allows preparing phthalimides via C–H/N–H activation from corresponding aromatic amides. This reaction tolerates a variety of functional groups in which the C–H bonds of electron-rich aromatic amides are favored.



Scheme 6.23 Rhodium-catalyzed carbonylative C–H activation



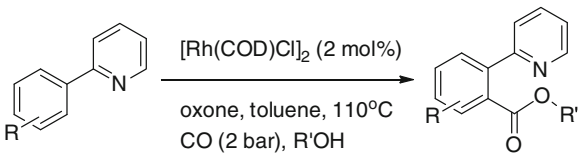
Scheme 6.24 Rhodium-catalyzed C–H activations

Over the past decades, Murai's and Chatani's groups developed a series of methodologies for the rhodium-catalyzed carbonylations initiated by C–H activation [73–76]. A range of heterocyclic compounds, such as *N*-acylpiperazines, *N*-(2-pyridinyl)piperazines, 2-arylpyridines, and *N*-arylpyrazoles, were acylated with CO and ethylene (Scheme 6.24).

Zhang and colleagues described a rhodium-catalyzed oxidative carbonylation of aromatic C–H bond with CO and alcohols in 2009 (Scheme 6.25) [77]. A broad substrate scope of electron-rich, electron-poor, and heterocyclic arenes were carbonylated under their conditions and produced the corresponding esters in good yields. The reaction is tolerant with many functional groups, and excellent regioselectivities and yields up to 96 % of *o*-substituted aryl or heteroaryl carboxylic esters were achieved by this method. A possible mechanism for the rhodium-catalyzed oxidative carbonylation reaction was also proposed by the authors. Among all the oxidants evaluated, oxone provided the best results in this reaction.

In this chapter, the transition of metal catalyzed carbonylative activation of C–H bonds has been discussed. This area is dominated by Pd, Ru and Rh catalysts, whereas the ability of other metals, such as Cu and Fe, have still not been explored. From the reaction mechanism point of view, the first step is the palladation of arene to produce an Ar-Pd bond, and then be followed by CO insertion.

Scheme 6.25 Rhodium-catalyzed C–H activation of phenylpyridines



In the next chapter we will discuss the carbonylative Heck reaction. Again, the reaction mechanism is different from those in the preceding chapters.

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