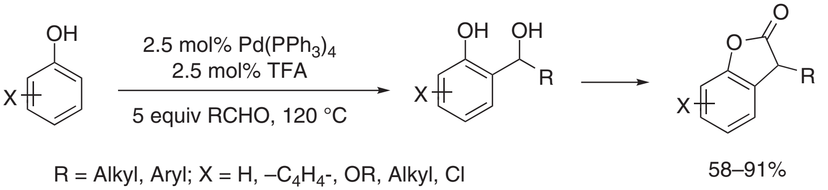
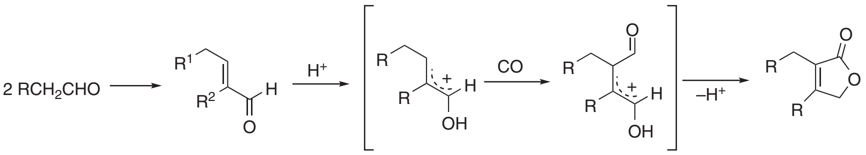


Scheme 1.131 Cyclocarbonylation to furanones. Source: Satoh et al. [301]; Satoh et al. [302].



Scheme 1.132 Acid-mediated conjugate carbonylation.

absence of PPh_3 or HCl, and high yields could be achieved with alkanols as a solvent (e.g., EtOH). After decarboxylation of the resultant phenylmalonate, the desired phenylacetic acid derivative in 70–75% yield can be obtained.

1.8 Oxidative Carbonylation Reaction

Oxidative carbonylations have acquired a growing importance during the last few years, owing to the development of new and selective catalytic systems, mainly based on palladium, which are able to promote ordered sequences of transformations under mild conditions with formation of highly functionalized carbonyl compounds in one step starting from simple building blocks [305–307].

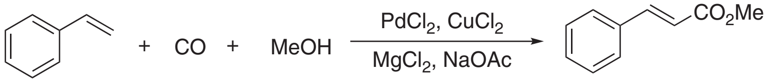
1.8.1 Oxidative Carbonylation of Alkenes

In 1963, Tsuji et al. reported the reaction of olefin–palladium chloride complexes with CO and alcohols to produce β-chloroacyl chlorides for the first time [308, 309]. Using internal and terminal aliphatic olefins under 4–10 MPa CO pressure, the corresponding chloroesters in 5–41% yields were transformed.

In 1969, Yukawa and Tsutsumi reported the reaction of a styrene–palladium complex with CO in alcohols [310]. Various cinnamates and phenylsuccinates were synthesized with up to 41% yield.

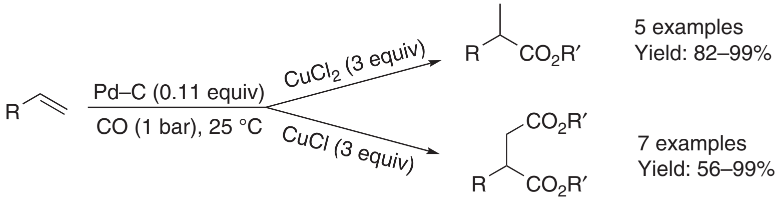
In 1979, Cometti and Chiusoli published their results on the synthesis of methyl cinnamates from styrene [311]. Using a mixture of $PdCl_2$, $CuCl_2$, $MgCl_2$, and NaOAc, the reaction was run in methanol at room temperature under atmospheric pressure of CO to produce methyl cinnamate with up to 80% selectivity together with dimethyl phenylsuccinate as products (Scheme 1.133).

In 1990, Inomata et al. reported the Pd/C-catalyzed oxidative carbonylation of terminal olefins [312]. The reaction proceeded selectively to mono- or diesters under



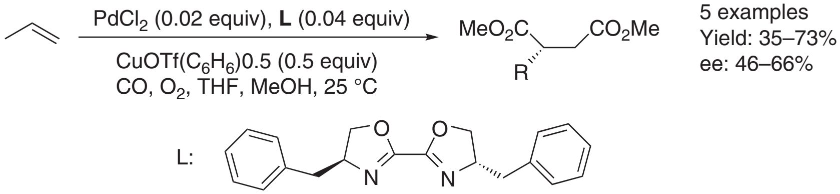
Scheme 1.133 Palladium-catalyzed synthesis of methyl cinnamate.

1 bar of CO at room temperature in good yields in the presence of $CuCl_2$ or CuCl as an additive. Interestingly, mainly monoesters were observed in 82–99% yields if $CuCl_2$ was applied as an oxidant, whereas diesters were formed in 56–99% yields by using CuCl as the oxidizing reagent (Scheme 1.134).



Scheme 1.134 Pd/C-catalyzed oxidative carbonylation of alkenes.

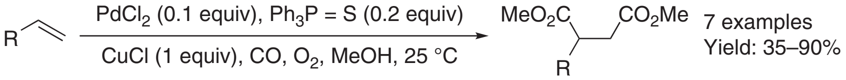
Later, an asymmetric version for the synthesis of diesters was published by Inomata and coworkers [313]. By using a chiral bisoxazoline ligand in the presence of Cu^I triflate at room temperature, terminal olefins were carbonylated to enantiomerically enriched diesters in 35–73% yields with up to 66% ee (Scheme 1.135).



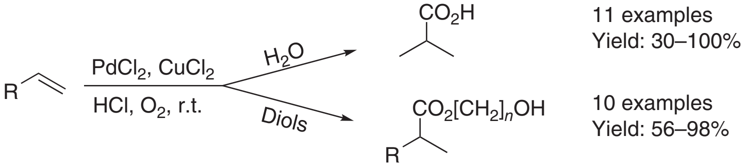
Scheme 1.135 Palladium-catalyzed oxidative carbonylation of olefins.
Tf = trifluoromethanesulfonate.

In 1998, Saigo and coworkers reported the use of phosphine sulfides as ligands for the oxidative carbonylation of olefins [314]. Diesters were produced in 35–90% yields starting from the corresponding alkenes at room temperature (Scheme 1.136). Enantioselectivity can be obtained by applying chiral biphosphine sulfides as ligands. Notably, their model system gave rise to 36% and 60% yield in the absence of a ligand and with triphenylphosphine oxide, respectively. However, no reaction occurred in the presence of PPh_3.

Alper and coworkers reported another protocol for the hydroxycarbonylation of alkenes [41]. When $PdCl_2$ and $CuCl_2$ were applied as the catalytic system, alkenes were transformed into branched propionic acids in 30–100% yields in the presence of water, oxygen, and HCl. Later, they extended their protocol to the



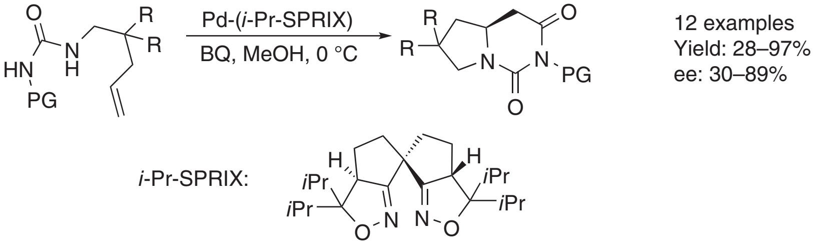
Scheme 1.136 Palladium-catalyzed oxidative carbonylation of olefins using triphenylphosphine sulfide as a ligand.



Scheme 1.137 Palladium-catalyzed oxidative carbonylation of alkenes to branched products.

monohydroesterification of diols [315]. Under 1 bar of CO and at room temperature, the products could be yielded in 56–98% (Scheme 1.137).

Sasai and coworkers published the enantioselective oxidative carbonylation of alkenylureas. By using the PE-spiro bis(isoxazoline) system, the desired products were produced in 28–97% yields and with 30–89% ee (Scheme 1.138) [316].

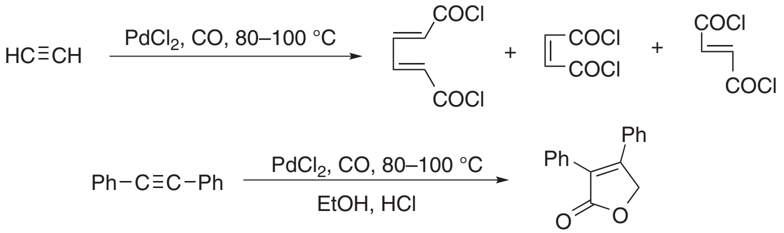


Scheme 1.138 Palladium-catalyzed oxidative carbonylation of alkenylureas. PG = protecting group. Source: Modified from Jamison et al. [116].

The oxidative carbonylation of alkenes has been used in many applications in total synthesis [317–320], but most of the work has focused on ligands and catalyst systems. In general, large amounts of excess copper salts or other organic oxidants are still required. This has an impact on the environment, and the separation of products is difficult. Therefore, the important goal in the future is to utilize air, oxygen, or hydrogen peroxide as "green oxidants" under mild conditions.

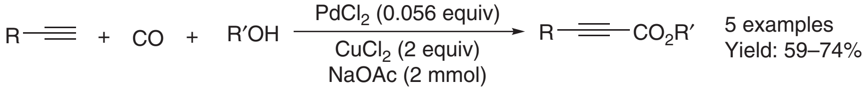
1.8.2 Oxidative Carbonylation of Alkynes

The first example of oxidative carbonylations of alkynes was reported in 1964. Tsuji et al. demonstrated the palladium-mediated transformation of acetylene into muconyl, fumaryl, and maleic acid chloride (Scheme 1.139) [321]. Later, they used diphenylacetylene as a substrate for the synthesis of lactones in the presence of alcohol and HCl [322].



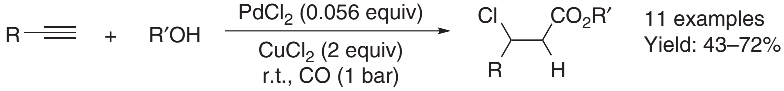
Scheme 1.139 Palladium-mediated oxidative carbonylation of alkynes. Source: Modified from Tsuji et al. [321].

Tsuji et al. further developed the palladium-catalyzed oxidative carbonylation of terminal acetylenes. For example, acetylenecarboxylates were produced in 59–74% yields at room temperature under atmospheric pressure of CO, but stoichiometric amounts of $CuCl_2$ were needed to reoxidize Pd^0 (Scheme 1.140) [69].



Scheme 1.140 Palladium-catalyzed oxidative carbonylation of acetylenes to acetylenecarboxylates. Source: Modified from Tsuji et al. [69].

Jiang and coworkers described the synthesis of 3-chloroacrylate esters [323]. The reaction proceeded under 1 bar of CO at room temperature yielding 30–72% of the desired products in a highly regio- and stereoselective manner (Scheme 1.141).

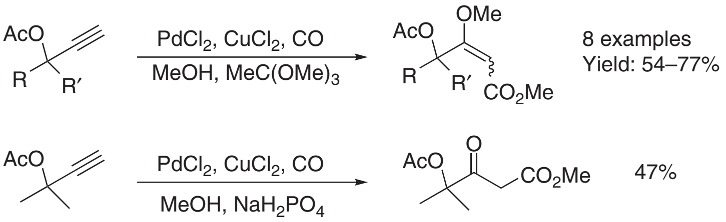


Scheme 1.141 Palladium-catalyzed oxidative carbonylation of acetylenes to chloroacrylates.

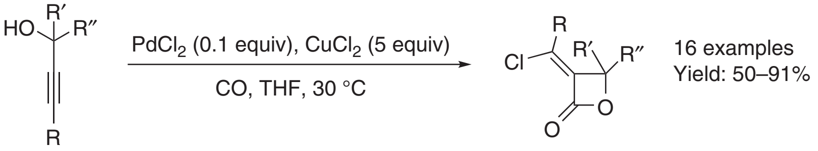
The oxidative carbonylation of 1,1-disubstituted propargyl acetates to unsaturated esters was developed by Okumoto et al. in 1999 [324]. Stoichiometric amounts of $CuCl_2$ were used as the oxidant, and the reaction had to be conducted at 0 °C (Scheme 1.142).

A mild and efficient methodology for the palladium-catalyzed carbonylative synthesis of four-membered β-lactones has been published by Ma et al. [325]. In the presence of $PdCl_2$ and $CuCl_2$, β-lactones were produced from 2-alkynols in good yields (Scheme 1.143). Using readily available optically active propargylic alcohols, the corresponding b-lactones were generated with high ee.

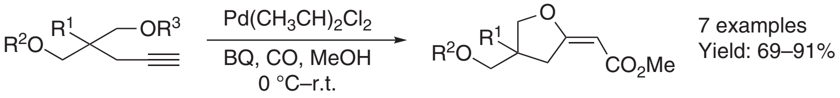
Moreover, an improved method for the oxidative carbonylation of hydroxyalkynes was developed by Kato et al. [326]. Applying $Pd(MeCN)_2Cl_2$ (0.05 equiv) and 1.1 equiv of BQ in methanol at 0 °C under 1 bar of CO, the desired products were



Scheme 1.142 Palladium-catalyzed oxidative carbonylation of propargylic acetates.



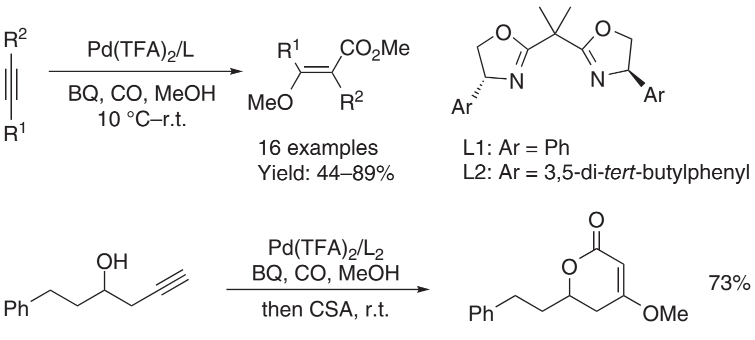
Scheme 1.143 Palladium-catalyzed oxidative carbonylation of alkynes to β-lactones.



Scheme 1.144 Palladium-catalyzed oxidative carbonylation of alkynes to furans.

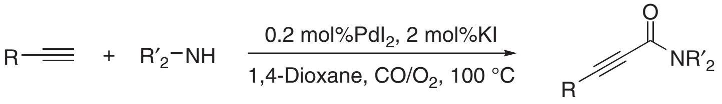
obtained from the corresponding cyclic- and acyclic-4-yn-1-ols in 69–91% yields (Scheme 1.144).

In 2009, Kato et al. applied their Pd^{II} bis(oxazoline) complexes in the intermolecular methoxycarbonylation of terminal alkynes. Terminal alkynes were transformed into β-methoxyacrylates in good yields (Scheme 1.145) [327]. In addition, this methodology was applied in the total synthesis of annularin G and annularin H [328].



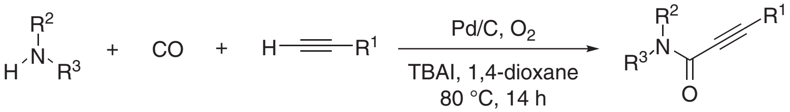
Scheme 1.145 Palladium/BQ-catalyzed oxidative carbonylation of alkynes. CSA = (+)-10-camphorsulfonic acid. Source: Modified from Kato et al. [327].

In 2001, Gabriele and Salerno reported the first catalytic aminocarbonylation of alk-1-ynes [329]. Using a 4 : 1 CO : air mixture (20 atm total pressure), both alkyl- and arylacetylenes could be converted to the corresponding 2-ynamides in 42–80% yields successfully and the latter were more reactive substrates (Scheme 1.146).



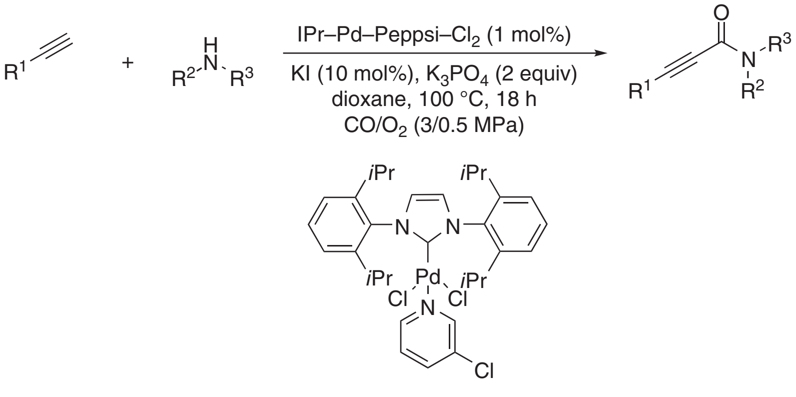
Scheme 1.146 Palladium-catalyzed oxidative aminocarbonylation of alk-1-ynes.

In 2012, Bhanage and coworkers presented Pd/C-catalyzed oxidative aminocarbonylations of alk-1-ynes that is applicable for the synthesis of a wide range of biologically active alk-2-ynamide derivatives (Scheme 1.147). Under the mild conditions, secondary amines provide the corresponding alk-2-ynamides in 55–94% yields [330]. The catalyst can reuse for up to four consecutive cycles.



Scheme 1.147 Pd/C-catalyzed oxidative aminocarbonylation of alk-1-ynes.

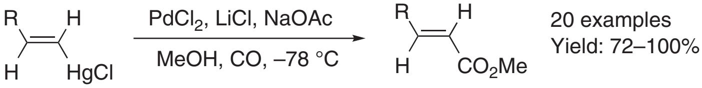
In 2015, Xia and Liu described palladium–NHC catalytic system that allows the direct formation of a range of 2-ynamides from commercially available alkynes via oxidative aminocarbonylation (Scheme 1.148) [331]. Under 3 MPa CO, 0.5 MPa O_2 and at 100 °C, the corresponding products in 50–95% yields can be obtained. They also prove that amido-Pd could be transformed into amido-Pd-alkynyl in this efficient process.



Scheme 1.148 Palladium–NHC-catalyzed oxidative aminocarbonylation of alkynes. Source: Zhang et al. [331].

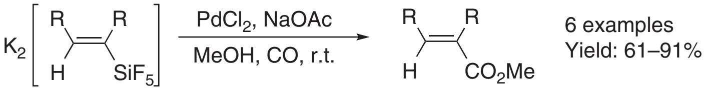
1.8.3 Oxidative Carbonylation of Organometallic Reagents

In 1974, Stille and Wong published the first oxidative carbonylation based on organomercury compounds [332]. Using stoichiometric amounts of $PdCl_2$, LiCl, and NaOAc, stereoselective carbonylation occurred at room temperature. However, the desired products were obtained only in low yield. Larock improved the methodology by conducting the reaction at −78 °C [333]. Unsaturated carboxylic acids and esters were formed in 72–100% yields starting from the corresponding vinylmercurials. Although stoichiometric amounts of palladium were still necessary, a catalytic version was realized by addition of a large excess of $CuCl_2$ (Scheme 1.149).



Scheme 1.149 Palladium-promoted carbonylation of organomercuries.

In 1979, Tamao et al. published concerning the oxidative carbonylation of organosilanes [334]. The reaction was carried out at room temperature and under 1 bar of CO, but stoichiometric amounts of $PdCl_2$ were required to form 61–91% of the corresponding vinyl esters (Scheme 1.150).



Scheme 1.150 Palladium-promoted carbonylation of organosilanes.

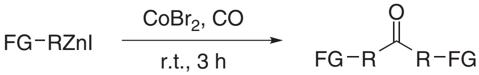
Lei and coworkers developed the first example of palladium-catalyzed oxidative carbonylation of organoindium reagents to produce different esters with desyl chloride as an oxidant [335]. Primary and secondary alkyl indium reagents as well as aryl indium reagents were carbonylated at 60 °C in the presence of catalytic amounts of palladium as a catalyst. The corresponding esters were formed in 60–96% yields, and the methodology showed broad functional group tolerance (Scheme 1.151).

$$Ar_2InCl \xrightarrow[\text{Desyl chloride, NEt}_3\text{, EtOH, CO, 60 °C}]{\text{PdCl}_2\text{(dppf) (5 mol\%)}} ArCO_2Et$$

21 examples
Yield: 60–96%

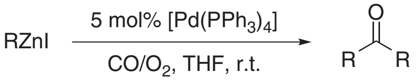
Scheme 1.151 Palladium-catalyzed carbonylation of organoindiums. DPPF = 1,1′-bis(diphenylphosphino)ferrocene.

In 1995, Knochel and coworker reported the oxidative carbonylation of organozinc reagents to produce symmetric ketones in the presence of stoichiometric cobalt bromide (Scheme 1.152) [336].A series of alkyl and aromatic symmetric ketones were prepared in 56–80% yields at room temperature.



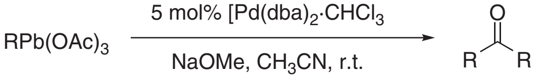
Scheme 1.152 Stoichiometric $CoBr_2$-mediated oxidative carbonylation of organozinc reagents. FG = functional group. Source: Modified from Devasagayaraj and Knochel [336].

Then, Jackson and coworkers reported the palladium-catalyzed oxidative carbonylation of organozinc reagents using O_2 as the oxidant (Scheme 1.153) [208]. Under 1 atm pressure of CO, the corresponding symmetric ketones with up to 84% yield can be obtained at room temperature.



Scheme 1.153 Palladium-catalyzed oxidative carbonylation of organozinc reagents. Source: Modified from Jackson et al. [208].

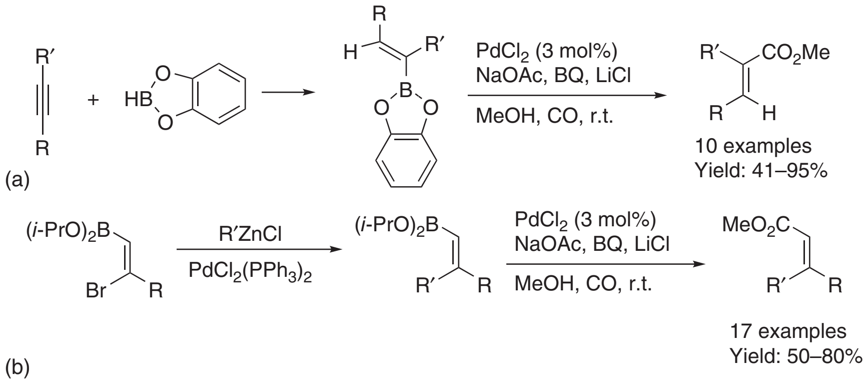
Kang and coworkers found oxidative carbonylation of organolead reagents was also employed to produce symmetric ketones (Scheme 1.154) [337]. In the presence of $Pd_2(dba)_3{\cdot}CHCl_3$ (5 mol%) and NaOMe (5 equiv) in CH_3CN under atmospheric pressure of CO at room temperature, organolead acetates can be carbonylated to afford symmetrical ketones with wide range of functional groups including heterocycles in 69–85% yields. Notably, the organolead compounds acted as both nucleophiles and oxidants, and the authors proposed that $RPb(OMe)_3$ was formed as a key intermediate.



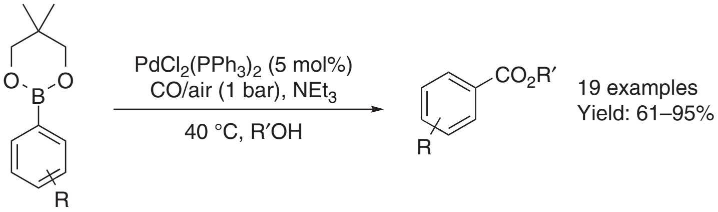
Scheme 1.154 Palladium-catalyzed oxidative carbonylation of organolead reagents. dba=dibenzylideneacetone. Source: Modified from Kang et al. [337].

Suzuki and coworker reported the palladium-catalyzed oxidative carbonylation of alkenylboranes as early as 1981. They prepared 1-alkenylboranes through hydroboration of alkynes, and subsequent oxidative carbonylation mediated by catalytic amounts of $PdCl_2$ in the presence of NaOAc and BQ in methanol provided unsaturated esters in good yields (Scheme 1.155a) [338]. Later, a stereoselective synthesis of β-mono and β,β-disubstituted α,β-unsaturated esters was established through a stepwise cross-coupling alkylation followed by an oxidative carbonylation of 2-bromo-1-alkenylboranes (Scheme 1.155b) [339]. Good yield and excellent stereoselectivity were achieved.

Lei and coworkers discovered a new protocol making use of air as an oxidant at low temperature [340]. Using a balloon pressure of a CO/air mixture, arylboronates were converted into the corresponding esters in 61–95% yields (Scheme 1.156). This was the first example of simply applying air in the oxidative carbonylation of organoboron compounds with alcohols.



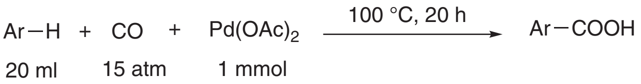
Scheme 1.155 Palladium-catalyzed oxidative carbonylation of alkenylboranes. Source: Modified from Miyaura and Suzuki [338]; Modified from Yamashina et al. [339].



Scheme 1.156 Palladium-catalyzed oxidative carbonylation of arylboronates using air.

1.8.4 Oxidative Carbonylation of Arenes

In 1980, Fujiwara et al. reported for the first time a palladium-mediated oxidative carbonylation of arenes to benzoic acids (Scheme 1.157) [341]. The direct carbonylation of benzene, toluene, anisole, chlorobenzene, furan, and thiophene was performed under CO and in the presence of Pd(OAc)$_2$. 2–43% of the corresponding benzoic acids were formed as the terminal products.



$$\underset{\text{20 ml}}{\text{Ar—H}} + \underset{\text{15 atm}}{\text{CO}} + \underset{\text{1 mmol}}{\text{Pd(OAc)}_2} \xrightarrow{\text{100 °C, 20 h}} \text{Ar—COOH}$$

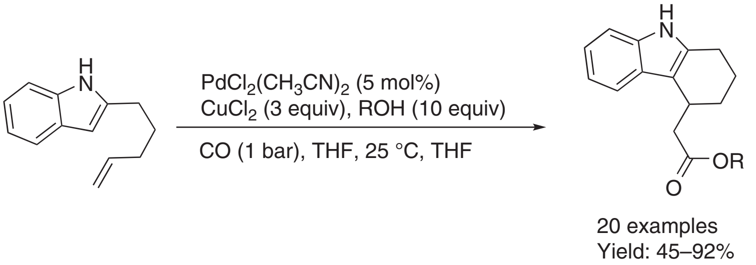
Scheme 1.157 Stoichiometric amounts of Pd(OAc)$_2$ for mediation of the oxidative carbonylation of simple arenes. Source: Modified from Fujiwara et al. [341].

Later, Fujiwara and coworkers developed a more powerful catalytic system (Scheme 1.158) [342, 343]. 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 oxidant in TFA at room temperature under an atmosphere of CO. The aromatic carboxylic acids were formed in good yields.

$$\mathrm{Ar{-}H} + \mathrm{CO} \xrightarrow[\mathrm{K_2S_2O_8,\ TFA,\ r.t.}]{\mathrm{Pd(OAc)_2}} \mathrm{Ar{-}COOH}$$

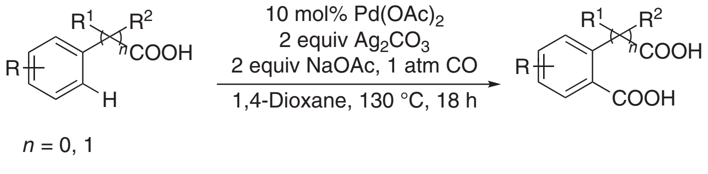
Scheme 1.158 $Pd(OAc)_2$/TFA-catalyzed oxidative carbonylation of simple arenes. Source: Lu et al. [342]. Taniguchi et al. [343].

Widenhoefer and Liu succeeded in palladium-catalyzed oxidative carbonylations for the synthesis of tetrahydrocarbazoles [344, 345]. 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 45–92% yields with high regioselectivity (Scheme 1.159).



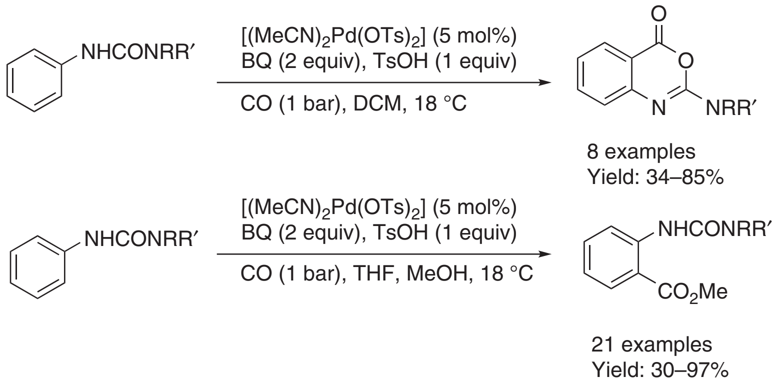
Scheme 1.159 Palladium-catalyzed cyclization/alkoxycarbonylation of alkenyl indoles.

In 2008, Yu and coworker subsequently reported the Pd^{II}-catalyzed direct carboxylation of benzoic and phenylacetic acid derivatives to form dicarboxylic acids (Scheme 1.160) [346]. In the presence of Ag_2CO_3 as an oxidant, 40–93% yields of dicarboxylic acids can be obtained at 130 °C with 1 atm CO. They also characterized the first cyclometalation complex formed from carboxylic acids by X-ray crystallography.



Scheme 1.160 $Pd(OAc)_2$-catalyzed oxidative carbonylation of benzoic and phenylacetic acid. Source: Giri and Yu [346].

Booker-Milburn and Lloyd-Jones published an interesting oxidative carbonylation of aniline derivatives [347]. The reaction proceeded under 1 bar of CO at room temperature with 5 mol% of $[Pd(OTs)_2(MeCN)_2]$ as a precatalyst. Cyclic imidates in 34–85% yields and methyl anthranilates in 30–97% yields can be obtained (Scheme 1.161). Notably, different products can be achieved by simply changing the reaction conditions, such as solvents.



Scheme 1.161 Palladium-catalyzed oxidative carbonylation of aniline derivatives.

1.8.5 Oxidative Carbonylation of Amines

The palladium-catalyzed oxidative carbonylations of amines to ureas were described for the first time by Tsuji and Iwamoto in 1966 [348]. With *n*-decylamine (7.9 g) and palladium chloride (0.5 g) in benzene (30 ml) at 180 °C for 20 hours with shaking, *N*,*N*′-didecyloxamide (3.8 g) and 1,3-didecylurea (2.2 g) were obtained.

In 2001, Deng and Shi reported the first gold(I) complex-catalyzed oxidative carbonylation of amines for the syntheses of carbamates (Scheme 1.162) [349]. At 200 °C and 5 MPa of initial total pressure, 34–100% conversions and 35–93% selectivities can be obtained. Then, they prepared polymer-immobilized gold catalysts ($HAuCl_4{\cdot}4H_2O$) for the oxidative carbonylation of aniline and its derivatives [350]. Carbamates and symmetric ureas with up to 99% selectivity can be obtained at 175 °C with 5.0 MPa mixed gases (CO of 99.99% purity at 4.0 MPa and O_2 of 99.99% purity at 1.0 MPa).

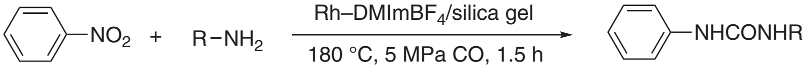
$$\mathrm{R(NH_2)}_n + \mathrm{CO} + \mathrm{O_2} + \mathrm{R'OH} \xrightarrow[\text{200 °C, 3 h}]{[\mathrm{Au(PPh_3)}_x]_y\mathrm{Z},\ \mathrm{PPh_3}} \mathrm{R(NHCO_2R')}_n + \mathrm{H_2O}$$

R = Ph, alkyl
$R' = CH_3, CH_3CH_2$
n = 1 or 2; x,y = 1 or 2
$Z = Cl, NO_3, S$

Scheme 1.162 Gold(I) complex-catalyzed oxidative carbonylation of amines. Source: Shi and Deng [349].

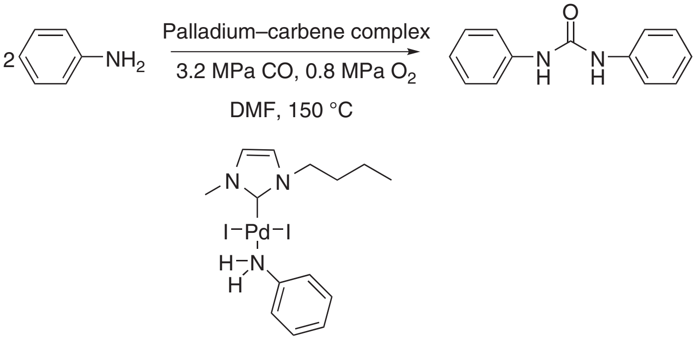
In 2001, Deng and Shi also found a novel $PdCl_2/ZrO_2–SO_4^{2-}$ catalyst for the synthesis of carbamates by oxidative carbonylation of amines [351]. For example, under O_2/CO (MPa) = 0.7/3.3 and at 170 °C, β-naphthylamine was oxidatively carbonylated, almost 100% conversion and 95% selectivity could be achieved as the reaction proceeded in only 15 min. Then, they developed palladium complex–IL catalyst system for the carbonylation of amines to give carbamate or urea [352]. When using $BMImBF_4$ as IL, under 4.0 MPa CO and 1.0 MPa O_2 at 175 °C, 99% conversion of aniline and 98% selectivity of methyl phenylcarbamate with 4540 h^{-1} TOF can be observed. In addition, IL-containing $Pd(phen)Cl_2$ could also be recovered and reused.

In 2005, Deng and Shi prepared silica gel confined IL containing a metal complex ($HRu(PPh_3)_2Cl_2$, $Rh(PPh_3)_3Cl$, $Pd(PPh_3)_2Cl_2$, and $Co(PPh_3)_3Cl_2$) as heterogenized catalysts for the carbonylation of amines and nitrobenzene without molecular oxygen to afford the corresponding ureas (Scheme 1.163) [353]. For example, when using Rh–$DMImBF_4$/silica gel as a catalyst, 92% conversion of aniline and 98% selectivity of disubstituted ureas with 11 548 h^{-1} TOF can be observed.



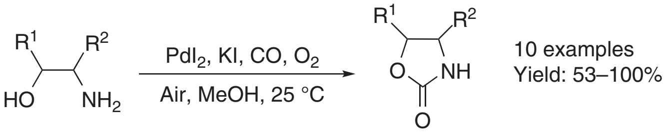
Scheme 1.163 Rh–$DMImBF_4$/silica gel-catalyzed oxidative carbonylation of amines. Source: Modified from Shi et al. [353].

In 2007, Xia and coworkers demonstrated that oxidative carbonylations of amines to ureas are also catalyzed by supported N-heterocyclic carbine (NHC)–palladium complexes (Scheme 1.164) [354, 355]. They showed that the palladium–carbene complex containing both an aniline and an NHC ligand was the active species for this oxidative carbonylation of amines. Without any promoter, various ureas were produced in 46–99% yields. Other immobilized palladium nanoparticles and water-soluble palladium catalysts were also presented [356, 357].



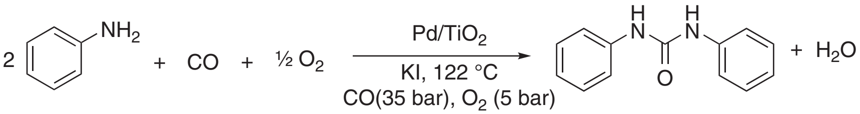
Scheme 1.164 One example of palladium–carbene-catalyzed oxidative carbonylation of amines. Source: Zheng et al. [354]; Zheng et al. [355].

In 2010, Giannoccaro et al. reported $L_nPdCl_2/NEt_3{\cdot}HI$ (L = 2,2′-dipyridine (dipy), 2-(β-diphenylphosphine)ethylpyridine (PN), PPh_3, CH_3CN)-catalyzed oxidative carbonylation of amino alcohols to *N*,*N*′-bis(hydroxyalkyl)ureas under mild conditions (30–60 °C, $P(CO/O_2)$ = 0.1 MPa) using molecular oxygen as the oxidant [358]. 74–96% substrate conversions and 67–90% urea isolated yields can be obtained. The catalytic system can be easily recovered and recycled at least six times. Interestingly, the related catalytic carbonylation of amino alcohols to 2-oxazolidinones was also published previously [359]. 53–100% yields of the corresponding products were obtained through direct PdI_2/KI-catalyzed oxidative carbonylation of readily available 2-amino-1-alkanols (Scheme 1.165).



Scheme 1.165 Palladium-catalyzed oxidative carbonylation of 2-amino-alcohols.

In 2019, Shi's group reported Pd/TiO_2 catalyst system for the oxidative carbonylation of amines to ureas with ultra-low Pd content under organic ligand- and solvent-free conditions (Scheme 1.166) [360]. Under 35 bar CO and 5 bar O_2, the corresponding ureas can be obtained in 30–88% yields with up to 250 000 h^{-1} catalytic TOFs (moles of amines converted per mole of Pd per hour) at 122 °C. This is the reported highest TOF numbers so far. In addition, Pd/TiO_2 catalyst can be recycled at least 10 runs without loss in catalytic activity.



Scheme 1.166 One example of Pd/TiO_2-catalyzed oxidative carbonylation of amines. Source: Modified from Liu et al. [360].

Some other metal-catalyzed oxidative carbonylation of amines with homogeneous transition metal/organic ligand complexes [361–367] and heterogeneous catalysts [368–370] were also studied.

1.9 Other Reactions

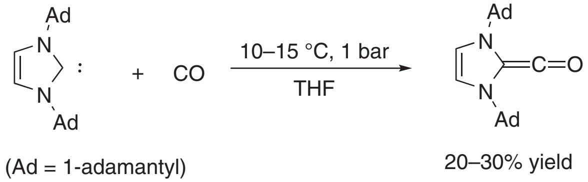
To explore other ways to use CO, the replacement of the diazo group in diazoalkanes by CO to afford the corresponding ketenes (Scheme 1.167) might be a synthetically useful reaction since ketenes are versatile intermediates in organic synthesis [371, 372].

(X, Y = H, alkyl, aryl, alkylthio, acyl, alkoxycarbonyl, alkylamino, F, Cl, trialkylsilyl, etc.)

Scheme 1.167 Replacement of the diazo group in diazoalkanes by carbon monoxide.

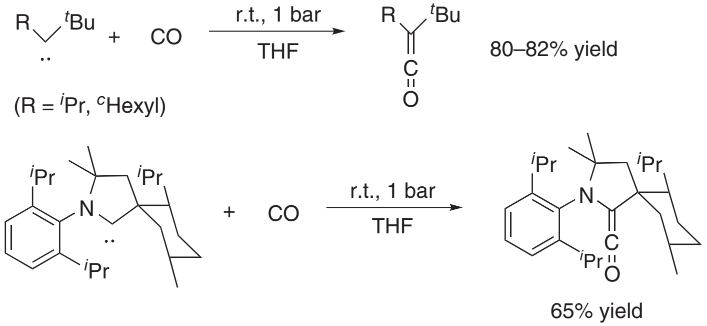
1.9.1 Reactions of Diazoalkanes with Carbon Monoxide

In 1994, Lyashchuk et al. reported the reactivity of stable imidazol-2-ylidenes toward CO. Under atmospheric pressure of CO, the synthesis of 1,3-di-1-adamantylimidazol-2-carbonyl from 1,3-di-1-adamantylimidazol-2-ylidene in 20–30% yield at 10–15 °C in THF solutions (Scheme 1.168) [373].



Scheme 1.168 Synthesis of 1,3-di-1-adamantylimidazol-2-carbonyl. Source: Modified from Lyashchuk and Skrypnik [373].

In 2006, Bertrand and coworkers described a smooth addition of CO at 1 bar pressure to the stable amino-substituted acyclic carbenes and a cyclic carbene at room temperature in THF, which resulted in the corresponding stable ketenes in 80–82% and 65% yields, respectively (Scheme 1.169) [374].

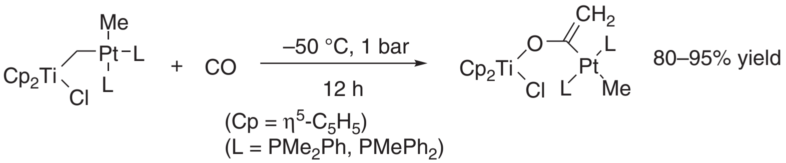


Scheme 1.169 Reactions of amino-substituted acyclic carbenes and a cyclic carbene. Source: Modified from Lavallo et al. [374].

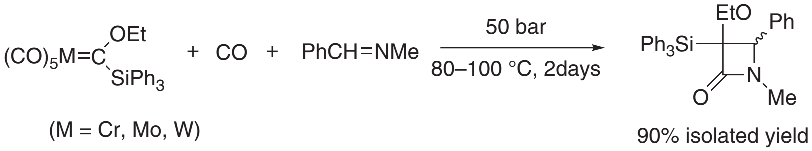
In 1989, Grubbs and coworkers found heterobinuclear complexes with *m*-methylene ligands $Cp_2Ti(Cl)CH_2Pt(CH_3)L_2$ (L = $P(CH_3)_2Ph$, PCH_3Ph_2) to react with CO at atmospheric pressure rapidly to give *m*-(C,O)-ketene species $Cp_2Ti(Cl)–OC(=CH_2)–Pt(CH_3)L_2$ in 80–95% yields (Scheme 1.170) [375].

Kron et al. reported ketene $Ph_3Si(EtO)C=C=O$ prepared in situ from the carbene complexes $(CO)_5M=C(OEt)SiPh_3$ (M = Cr, Mo, W) with 50 bar CO to react at 80–100 °C, among others, with *N*-methylbenzimine to give the corresponding β-lactam in 90% isolated yield (Scheme 1.171) [376].

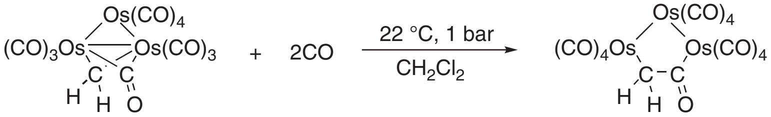
Geoffroy and coworkers reported the interconversion of methylene and ketene ligands on a triosmium cluster. It was found that a triosmium methylene complex in



Scheme 1.170 Heterobinuclear complexes with *m*-methylene ligands. Source: Modified from Ozawa et al. [375].



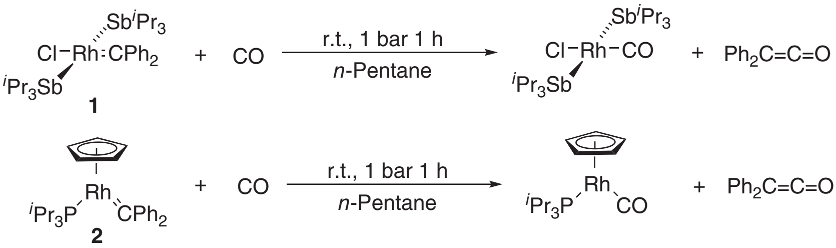
Scheme 1.171 Preparation of $Ph_3Si(EtO)C{=}C{=}O$. Source: Based on Kron and Schubert [376].



Scheme 1.172 Interconversion of methylene and ketene ligands. Source: Morrison et al. [377]; Morrison et al. [378].

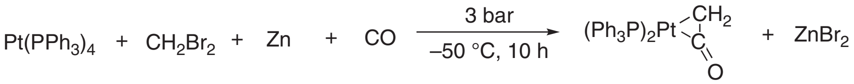
CH_2Cl_2 solution readily adds two moles of CO at 22 °C to yield 16–20% the ketene derivative (Scheme 1.172) [377, 378].

In 2000, Werner et al. reported carbonylation of the rhodium diphenylcarbene complexes **1** and **2** resulted in the formation of diphenylketene in 83–89% yields (Scheme 1.173). It was assumed that the diphenylketene is formed by carbon–carbon coupling in the coordination sphere of rhodium [379].



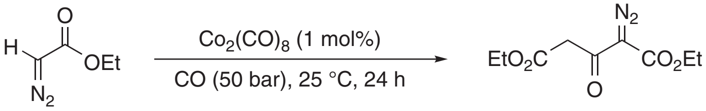
Scheme 1.173 Carbonylation of the rhodium diphenylcarbene complexes.

Miyashita et al. found the η2-(C,C)-ketene complex of platinum could be isolated in 23% yield from the reaction of $Pt(PPh_3)_4$ and CH_2Br_2 in the presence of zinc powder under 3 bar CO pressure (Scheme 1.174) [380].



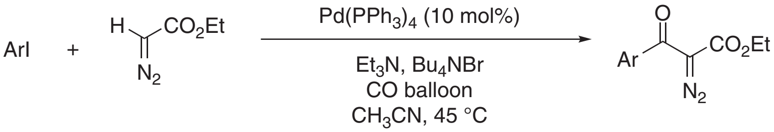
Scheme 1.174 Synthesis of the η^2-(C,C)-ketene complex of platinum. Source: Modified from Miyashita et al. [380].

Since 2003, Ungváry and coworkers have carried out systematic studies on $CO_2(CO)_8$-catalyzed carbonylation of ethyl diazoacetate [381, 382]. In the presence of 1 mol% $CO_2(CO)_8$ and under 50 bar pressure of CO at room temperature, ethyl diazoacetate (EDA) was converted to diethyl 2-diazo-3-oxoglutarate in 91% yield (Scheme 1.175).



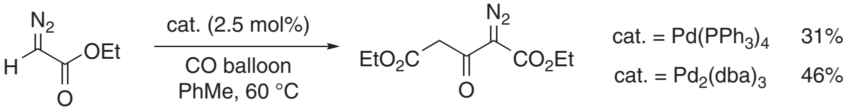
Scheme 1.175 $Co_2(CO)_8$-catalyzed carbonylation of ethyl diazoacetate.

In 2007, Wang and coworkers reported $Pd(PPh_3)_4$-catalyzed cross-coupling of aryl iodides with EDA [237]. Under atmospheric CO pressure, the carbonylation occurred to afford β-keto α-diazocarbonyl compounds in 43–66% yields at 45 °C (Scheme 1.176).



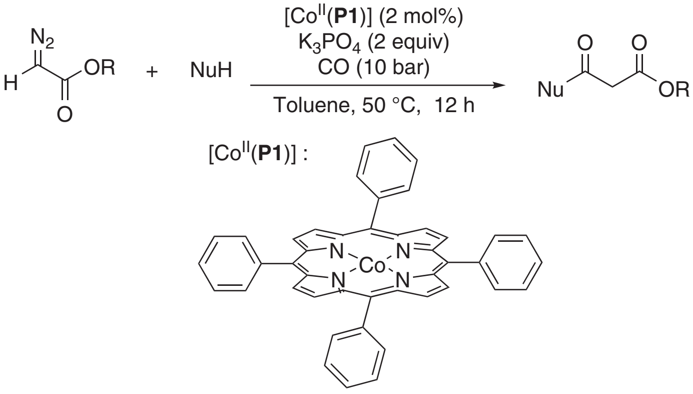
Scheme 1.176 $Pd(PPh_3)_4$-catalyzed cross-coupling of aryl iodides with EDA.

Later, Wang and Li found a comprehensive study of $Pd_2(dba)_3$-catalyzed carbonylation of diazo compounds [383]. In the initial study with EDA, similar results as in the $CO_2(CO)_8$-catalyzed system were observed with Pd(0) catalyst under atmospheric CO pressure (Scheme 1.177).



Scheme 1.177 $Pd_2(dba)_3$-catalyzed carbonylation of diazo compounds.

In 2013, de Bruin and coworkers reported cobalt(II)-porphyrin-catalyzed carbene carbonylation reactions (Scheme 1.178) [384]. Under 10 bar CO and at 50 °C, the β-ketoester products can be obtained in 53–75% yields when using CO, a-diazocarbonyl compounds and different nucleophiles.

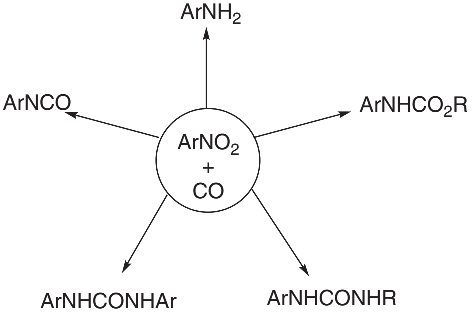


Scheme 1.178 [Co^{II}(Por)]-catalyzed β-ketoester synthesis. Source: Paul et al. [384].

In 2017, Sivasankar and Ramakrishna described that octacarbonyldicobalt as a nongaseous CO source catalyzed carbonylation of diazo compounds for the synthesis of amido esters and amido phosphonates [385]. When using 0.5 equiv $Co_2(CO)_8$ at room temperature, amido esters in 67–95% yields and amido phosphonates in 65–83% yields can be obtained.

1.9.2 Reaction of C–NO_2 with CO

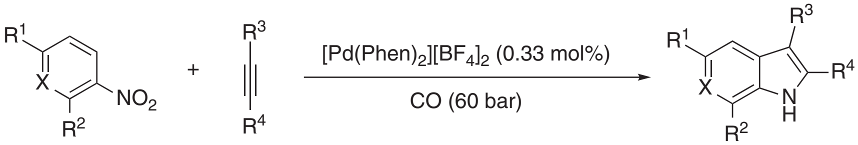
The catalytic carbonylation of nitro compounds is a field of great interest, as a number of important industrial products can be produced (Scheme 1.179) [386–388], such as the synthesis of isocyanates, carbamates, ureas, etc., which normally needed toxic phosgene as the reaction reagent and can be replaced by cheap CO.



Scheme 1.179 Carbonylation of nitro compounds. Source: Paul [386]; Tafesh and Weiguny [387].

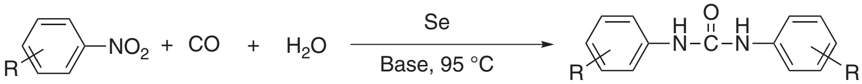
In 1990, the first isolation and characterization of a metallacyclic complex were performed [389, 390]. By combining $Pd(OAc)_2$, 1,10-phenanthroline (3 equiv), and $PhNO_2$ (40 equiv) and heating it in ethanol under CO (30 bar) at 80 °C, a yellow complex was precipitated, with 80% yield. PhNCO, $(PhNH)_2CO$, $(PhNHCO)_2NPh$, and CO_2 were produced by heating the complex in 1,2-dichlorobenzene under CO

(20 bar) at 170 °C. The addition of 2,4,6-trimethylbenzoic acid can increase the production of PhNCO. Finally, a mixture of the complex, $PhNO_2$, EtOH, under CO atmosphere, together with 2,4,6-trimethylbenzoic acid heated at 135 °C, 100% of the $PhNO_2$ was converted into $PhNHCO_2Et$ in 91% selectivity. Based on these studies, a reaction mechanism was given that was modified afterward for different product syntheses (Scheme 1.180).



Scheme 1.180 Reaction mechanism for Pd-catalyzed carbonylation of RNO_2.

Yu, Lu, and colleagues found that selenium can catalyze the carbonylation of nitroarenes to symmetrical 1,3-diarylureas under atmospheric pressure of CO [391]. In the presence of KOH or NaOAc as base, various ureas were produced with up to 94% yield in DMF at 95 °C (Scheme 1.181). They also reported a selenium-catalyzed reaction of nitroarenes and amides in the presence CO to *N*-arylamides [392]. Under the assistant of mixed organic bases NEt_3 and DBU (1,8-diazabicyclo[5.4.0]undec-7-ene), *N*-arylamides were produced in 41–88% yields by a selenium catalyst. Other catalytic carbonylation of organic nitro compounds can be found in reviews [386–388, 393].



Scheme 1.181 Selenium-catalyzed amide synthesis.