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Review

Structural and mechanistic studies of Pd-catalyzed C─C bond formation: The case of carbonylation and Heck reaction

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Abstract

The extraordinary catalytic activity of palladium in C─C bond forming processes is reviewed in respect to Heck and carbonylation reactions. Examples of catalytic systems based on palladium complexes with phosphorus ligands and phosphine-free systems and based on the Pd(0) colloid are presented. The two key steps of both reaction mechanisms: first, reduction of Pd(II) to Pd(0) complexes or Pd(0) colloids and second, oxidative addition of substrates (aryl or benzyl halides) are discussed.

Keywords: Palladium complexes; Palladium(0) colloid; C─C coupling; Heck reaction; Carbonylation reaction

1. Introduction

C─C bond formation reactions are fundamental reactions of organic chemistry. There are a number of excellent reviews and books covering different aspects of such processes and transition-metal-based homogeneous catalysts used for C─C bond forming reactions [1–9].

Among the many transition metal compounds, palladium complexes occupy a special place and have for many years been used as versatile tools in catalytic organic reactions. Scheme 1 presents examples of a broad application of palladium catalysts for organic synthesis, including reactions of industrial importance, such as ethylene chemistry.

Over 90 organic reactions are catalyzed with palladium, although most of them are not commercialized. The Wacker process, which delivers several million tons of acetaldehyde per year (converted mainly into acetic acid) is one of the simplest and most spectacular industrial applications of

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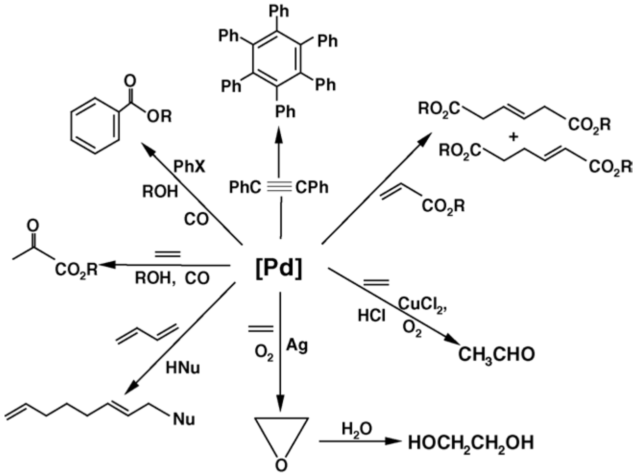
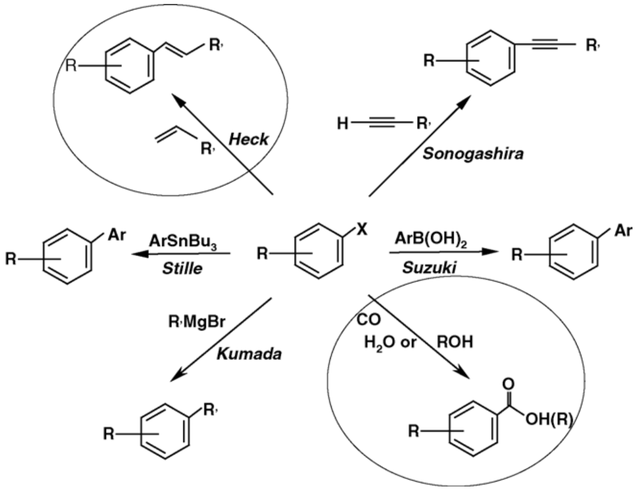


Scheme 1. Palladium catalyzed organic reactions.

palladium catalysts although recently this process has been replaced by methanol carbonylation. For about 50 years palladium compounds have been used as active and selective catalysts for reactions of many rather complicated substrates providing new useful synthetic organic products. Among those processes, palladium-catalyzed reactions with aryl halides as substrates are of particular importance (Scheme 2) [9]. Depending on the reaction conditions, aryl halides can be transformed into carboxylic acids, esters, or amides in a one-stage carbonylation process. Olefination of aryl halides, the so-called Heck reaction [1], produces functionalized olefins. In the Suzuki reaction bi-phenyl derivatives are obtained, and in the Sonogashira process phenylated alkynes are formed [1,6].

During the past 15 years palladium chemistry has become an extremely active part of coordination and organometallic chemistry related to broadly understood catalysis: homogeneous, heterogenized, heterogeneous, and, recently, nanocatalysis.



Scheme 2. Palladium catalyzed reactions of aryl halides [9].

This review has no ambition to cover all of the above-mentioned regions of catalysis and Pd-catalyzed reactions but to touch upon some problems of particular importance to our understanding of catalyst–structure–reactivity correlations and the mechanistic aspects of key Pd-catalyzed organic reactions. Those in our opinion can be exemplified by two reactions: carbonylation and Heck coupling (Scheme 2).

Both Heck and carbonylation reactions can be catalyzed by palladium complexes with phosphorus ligands in the coordination sphere or by phosphine-free (ligand-free) systems. Phosphorus ligands are usually used to stabilize Pd(0) complexes formed during the reaction course and prevent the formation of “palladium black”, considered catalytically inactive [10].

Recently, phosphine-free or ligand-free catalytic systems, economically profitable and environmentally friendly, have received increasing interest. According to our and other [7] recently reported studies, it seems most probable that in phosphine-free systems the key role is played by colloidal (soluble) forms of Pd(0) nanoparticles (Scheme 3). However, such colloidal catalytic systems require the presence of ammonium salts, polymers, or dendrimers as stabilizing agents. The absence of such a stabilizing medium leads to catalyst deactivation as a result of the transformation of the Pd(0) colloid into inactive “palladium black”. Generally, Pd(0) colloids are related to ligand-free (phosphine-free) systems, but it is not impossible that Pd(II) phosphine complexes, when used as catalyst precursors, can also undergo partial conversion into colloidal systems during long-lasting catalytic reactions (Scheme 3).

Recently published results concerning the Heck reaction with the participation of palladacycles seem to suggest the possibility of the presence of palladium nanoparticles in such systems [7,31].

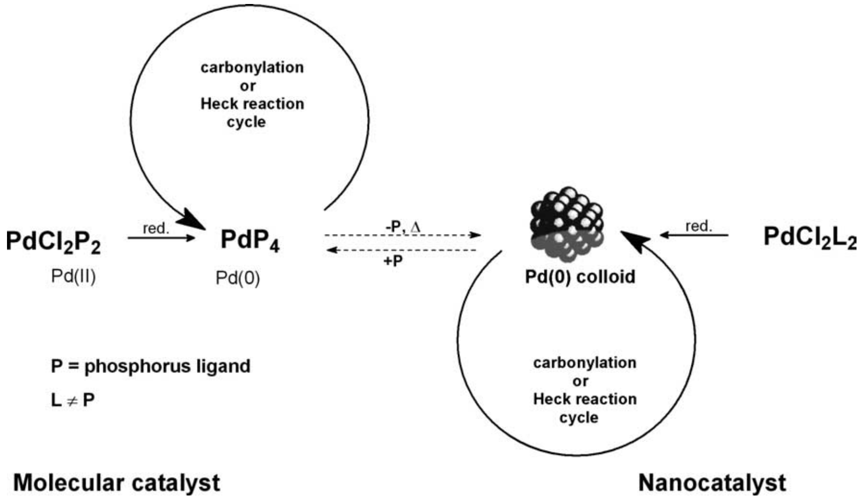
The formation of PdP_4-type monomolecular Pd(0) complexes (P = phosphorus ligand) from a Pd(0) colloid treated with an excess of the phosphorus ligand, suggested in Scheme 3, is hypothetical and requires experimental confirmation.

2. Formation of Pd catalysts

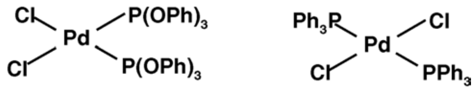
2.1. *Pd catalyst precursors with phosphorus ligands*

Palladium(II) complexes of the $PdCl_2P_2$ type are convenient catalysts precursors of Heck and carbonylation reactions. Depending on the steric properties of the coordinated phosphorus ligand (P), the complexes have *cis* (e.g. for $P = P(OPh)_3$, $P(OMe)_3$) or *trans* (e.g. for $P = PPh_3$, PCy_3) structures. Structural studies have confirmed that phosphorus ligands with a smaller steric hindrance, $\Theta < 140°$, prefer *cis* geometry (case of $P(OPh)_3$), whereas when $\Theta > 140°$, *trans* complexes are usually formed (case of PPh_3) (Scheme 4) [11].

Phosphites and phosphinites preferentially form *cis* isomers as has been X-ray confirmed for *cis*-$PdCl_2[P(OPh)_3]_2$



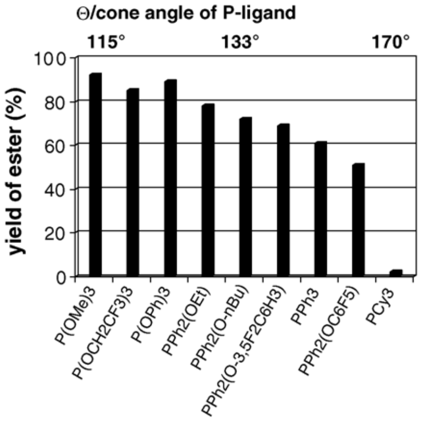
Scheme 3. Relation between monomolecular and nanosized palladium catalysts.



Scheme 4. *Cis*- and *trans*-isomers of $PdCl_2P_2$ complexes.

and *cis*-$PdCl_2[PPh_2(OEt)]_2$ [11]. Tests of the catalytic activity of $PdCl_2P_2$ complexes in methoxycarbonylation of benzyl bromide performed under mild conditions have shown a correlation between the phenylacetic acid methyl ester yield and the cone angle of the phosphorus ligand [11]. Palladium complexes with less crowded phosphorus ligands ($P(OMe)_3$, $P(OPh)_3$, $PPh_2(O^nBu)$) exhibit higher catalytic activity, producing ca. 90% of phenylacetic acid methyl ester (Scheme 5).

This is in agreement with the easier reduction of those complexes to Pd(0) species during treatment with CO and NEt_3 [11]. Therefore, the higher catalytic activity can be explained by the higher concentration of the active form of the catalyst, a Pd(0) complex, which activates benzyl bromide by an oxidative addition reaction.



1atm CO, 40°C, [Pd] 7 x 10^{-3} M, solvent: MeOH

Scheme 5. Effect of the phosphorus ligand cone angle on the yield of methoxycarbonylation of benzyl bromide with $PdCl_2P_2$ as the catalyst precursor [11].

Reactions of Pd(II) complexes containing π-acceptor phosphorus ligands (P) with NEt_3 in methanol under a CO atmosphere have produced different Pd(0) carbonyl-phosphine complexes identified by IR studies (Eq. (1)) [11]:

$$PdCl_2P_2 + CO + NEt_3 + MeOH \rightarrow$$

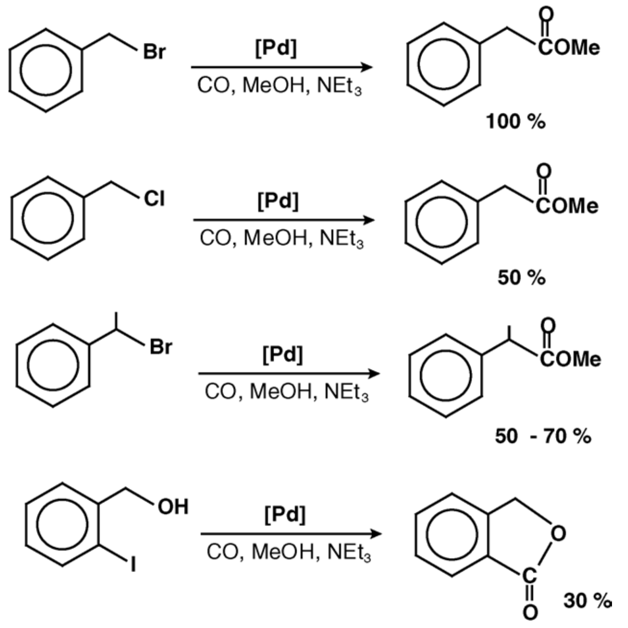
$$Pd(CO)_x(P)_y + HNEt_3Cl \quad (P = PPh_2(OEt), PPh_2(O^nBu),$$

$$P(OPh)_3, P(OCH_2CF_3)_3, P(OMe)_3), \quad x + y = 4 \qquad (1)$$

Unexpectedly good results have been obtained using palladium complexes with fluorinated phosphines ($PPh_x(C_6F_5)_{3-x}$, $x = 1$–2), which indicates that not only steric but also electronic effects of the phosphorus ligand are important in the carbonylation reaction [11].

Very convenient and frequently applied as a precursor is $Pd(OAc)_2$, often used together with an up to 20-fold excess of the free phosphorus ligand. Good results have also been achieved in the carbonylation reactions of aryl halides and benzyl chloride carried out in ionic liquids as the reaction medium [12]. The palladium catalyst, the ionic liquid phase was recycled after extraction of the products with water [12].

Palladium complexes with the $P(OPh)_3$ ligand have also been used in the carbonylation of benzyl alcohol in supercritical CO_2 [13], in methoxycarbonylation of benzyl bromide, benzyl chloride, and 1-bromoethylbenzene, as well as iodobenzyl alcohol (Scheme 6) [14]. The good catalytic activity of Pd-triphenylphosphite complexes makes it possible to perform these reactions with high yields under mild conditions [14]. In iodobenzene methoxycarbonylation to methyl benzoate, catalyzed with $PdCl_2[P(OPh)_2]_2$, a remarkable increase in reaction yield, up to 96% was achieved when $[^nBu_4N]Cl$ was introduced, both under 1 atm and under 5 atm of CO pressure [15].



Scheme 6. Examples of carbonylation reactions catalyzed by $PdCl_2[P(OPh)_3]_2$ catalyst precursor [14].

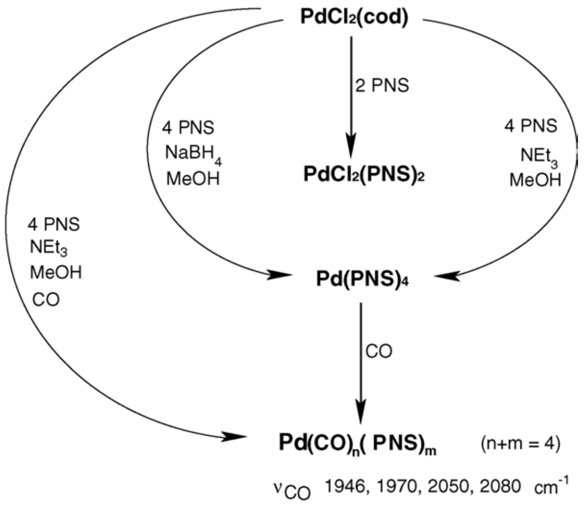
Replacement of hydrophobic phosphines by water-soluble ones significantly increases the effectiveness of contacts of transient forms with nucleophilic agents and additionally facilitates separation of organic products from water-soluble catalysts [16]. Several catalytic systems for carbonylation, based on water-soluble catalysts, have been described. The palladium complex of the formula $PdCl_2[PPh_2(m\text{-}C_6H_4SO_3Na)]_2$ has been applied as a catalyst for carbonylation of benzyl chloride, and 89–93% yield of phenylacetic acid was obtained at 1 atm of CO [17]. A palladium catalyst with TPPTS ($TPPTS = P(m\text{-}C_6H_4SO_3Na)_3$), formed in situ from $Pd(OAc)_2$ and TPPTS, catalyzes carbonylation of phenylbromide to benzoic acid. Spectroscopic studies confirm the participation of water-soluble palladium complexes like $Pd(TPPTS)_3$ in that catalytic process [18]. A Pd complex with TPPTS applied to the carbonylation reaction of aryl halides demonstrates very high TON, over 1500 [19,20]. Good results have also been obtained in the carbonylation of benzyl chloride with a system containing palladium compounds and a water-soluble phosphine, BINAS (BINAS = sulphonated 2,2′-bis(diphenylphosphino)-1,1′-binaphthyl), which was found active even in an acidic medium [20]. When $Pd(TPPTS)_3$ was applied as a carbonylation catalyst in water solution, phenylacetic acid was obtained from benzyl alcohol [21], and phenyl propionic acid was obtained from the styrene [22]. Other carboxylic acids are also the products of alcohol carbonylation, e.g. ibuprofen (2-(4-isobutylphenyl)propionic acid) has been obtained from 1-(4-isobutylphenyl)ethanol by applying $Pd(TPPTS)_3$ [23,24].

Palladium acetate ($Pd(OAc)_2$) and dichloride ($PdCl_2$) with the addition of TPPTS are very active catalysts in the Heck reaction of iodobenzene with butyl acrylate in a two-phase system (toluene–ethylene glycol) [25]. Good results have also been obtained with a supported aqueous-phase catalyst (SAPC), for which a stepwise increase in the reaction rate in successive catalytic cycles has been detected [25]. Supported on silica ethylene glycol phase Pd-TPPTS catalyst (Pd-SLPC) was used in the multiphase Heck reaction with very high recycling efficiency [25].

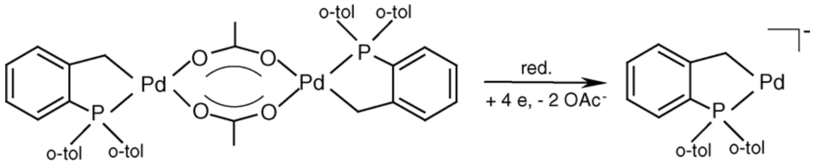
A catalytic system containing $PdCl_2(cod)$ (cod = 1,5-cyclooctadiene) and a water-soluble phosphine, PNS ($PNS = Ph_2PCH_2CH_2C(O)NHC(CH_3)_2CH_2SO_3Li$), in water/toluene solution exhibits activity in the carbonylation of benzyl bromide to benzeneacetic acid [26]. In reactions carried out in water/alcohol solution, corresponding esters have been obtained with yields dependent on the kind of alcohol used: 24% for BuOH, 62% for ^{i}PrOH, 78% for EtOH, and 85% for MeOH. The participation of a Pd(0) phosphine complex, $Pd(PNS)_4$, has been proven by means of $^{31}P\{^1H\}$ NMR and IR methods (Scheme 7) [26].

The same system has also been found to be active in the methoxycarbonylation of benzyl bromide under milder conditions, at 40–50 °C and 1 atm of CO [14]. The yield of phenylacetic acid methyl ester depends on the concentration of PNS. At the optimal concentrations of the reagents ($[NEt_3]:[PhCH_2Br] = 2.5$; $[PNS]:[Pd] = 4$) two experiments were performed in water and water/toluene, giving 76 and 68% of phenylacetic acid, respectively.

The dependence of the reaction yield on the NEt_3 and PNS concentration was explained as a result of their influence on the formation of a catalytically active form of a Pd(0) complex of the formula $Pd(PNS)_4$. In real catalytic reaction conditions in a CO atmosphere, a mixture of palladium-carbonyl-phosphine complexes represented by the formula $Pd(CO)_n(PNS)_m$ ($n + m = 4$), identified by IR (four ν_{CO} bands at 1946, 1970, 2050, 2080 cm^{-1}), has been proposed (Scheme 7) [26].



Scheme 7. Transformations of catalyst precursor ($PdCl_2(cod)$) into Pd(0) catalytically active species.



Scheme 8. The pattern of palladacycle reduction to Pd(0) ionic complex [30].

2.2. Palladacycles and Pd complexes with chelating P ligands

A cyclometallated complex formed in the reaction of $Pd(OAc)_2$ with sterically demanding tri-*ortho*-tolyl phosphine (Scheme 8) has been developed by Herrmann and applied very successfully to Heck reactions of activated and non-activated olefins [27,28]. The reaction mechanism of that very active catalytic system has been the subject of many discussions leading to two different catalytic cycles involving Pd(II)/Pd(IV) or Pd(0)/Pd(II) redox systems [29,30]. The first mechanism (Pd(II)/Pd(IV)) involves oxidative addition of aryl halides to a Pd(II) complex leading to a Pd(IV) species that participates in further reaction steps. The key stage in the second mechanism (Pd(0)/Pd(II)) was the structure proposed for the transient complex of Pd(0) with Pd–C and Pd–P bonds instead of a previously proposed complex with terminally bonded phosphine $[AcO–Pd–P(o\text{-}tol)_3]^-$ (Scheme 8) [30]. This ionic complex can be formed during a palladacycle reduction without Pd–C bond rupture [30].

However, the recent observation that Heck coupling of PhBr with *n*-butyl acrylate proceeds at similar rates when catalyzed by the Herrmann's palladacycle and when catalyzed by $Pd(OAc)_2$ has put a question mark over the role of palladium phosphine complexes as active forms of catalysts [31]. Additionally, ES-MS studies of the catalytic reaction mixture have shown that both in reactions catalyzed by $Pd(OAc)_2$ and in those catalyzed by palladacycles the only identified form of the catalyst is $PdBr_3^-$ and no phosphine-containing species have been identified [31]. Also the experimental results obtained for a cyclopalladated imine catalyst indicated "ligand-free" Pd species in the catalytic reaction [32]. On the other hand, a full characterization (X-ray) of Pd(IV) intermediate containing Pd–Ph bond suggests also the possibility that oxidative addition of iodobenzene to Pd(II) phosphapalladacycle has occurred [33].

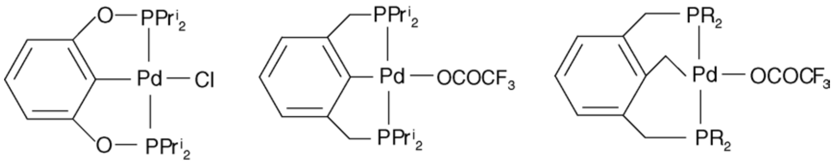
The phosphinito PCP palladium complex $PdCl\{C_6H_3\text{–}2,6\text{-}(OPPr_2{}^i)_2\}$ is a highly efficient catalyst for olefinic coupling of bromo and iodo compounds to disubstituted or trisubstituted alkenes [34]. Other palladium chelate complexes that demonstrate high catalytic activity are shown in Scheme 9 [35]. Catalytic systems consisting of palladium and ferrocenyl phosphines enables the carbonylation of aryl chlorides in very good yield [36,37]. The best results were obtained when 1-[2-(dicyclohexylphosphanyl)ferrocenyl]-ethyldicyclohexylphosphane was used. For those complexes, an unusual Pd(II)/Pd(IV) redox cycle has very often been proposed.

2.3. Phosphine-free Pd catalysts

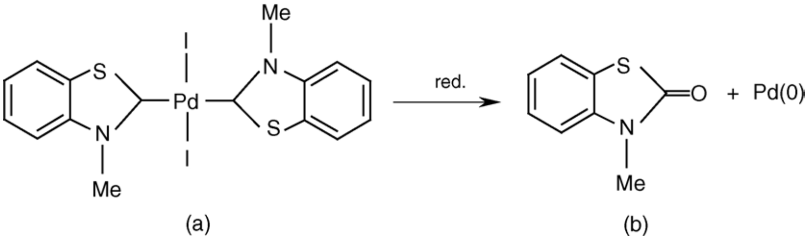
Phosphine-free (or ligand-free) Pd catalysts are active in the coupling of aryl iodites but not aryl bromides. However, the application of tertiary ammonium salts (like $[^nBu_4N]X$, X = Br, I) makes possible the coupling reaction of aryl bromide too [56,64].

A benzothiazole carbene complex of Pd(II) (Scheme 10(a)) has been found to be an efficient Heck reaction catalyst in the synthesis of cinnamates [38–41], as well as carbonylation of aryl halides in ionic liquids [42]. It was initially assumed that in this case, too, the reaction proceeds with the Pd(II)/Pd(IV) redox cycle and Pd(IV) complex formation is the result of oxidative addition of aryl halides to the starting Pd(II) complex. However, the reaction of that catalyst with tetrabutylammonium acetate, dissolved in tetrabutylammonium bromide, leads to fast formation of Pd(0) nanoparticles, which efficiently catalyze the formation of aryl cinnamic esters [38]. Careful analysis of the post-reaction mixture led to the isolation of 2-oxo-3-methylbenzothiazole (Scheme 10 (b)) as a product of ligand elimination from the coordination sphere of palladium during, most probably, its reductive decomposition with the participation of traces of water [38].

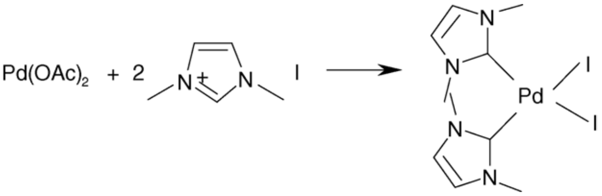
A ligand-free system based on the $PdCl_2(cod)$ complex has been found to be quite efficient in the methoxycarbonylation of iodobenzene, especially in the presence of $[^nBu_4N]Cl$. In reaction performed at 40 °C and 1 atm of CO in methanol, the yield of ester increased from 17 to 52% when $[^nBu_4N]Cl$ was added [15]. The 77–98% yields of ester were obtained



Scheme 9. Examples of PCP palladium complexes [34,35].



Scheme 10. Palladium(II) carbene complex reduction to Pd(0) colloid [38].



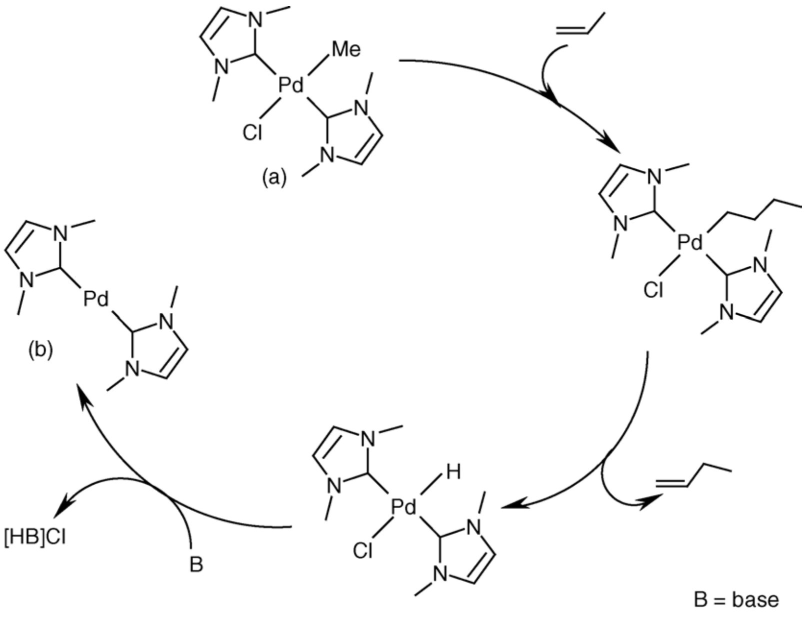
Scheme 11. Formation of bis-carbene Pd(II) iodite [44].

with the same catalyst at the presence of ammonium salts, [^{n}Bu$_4$N]X (X = Br, I, BF$_4$, PF$_6$) at 5 atm CO and 70 °C [15,43].

The family of phosphine-free catalysts also includes palladium complexes with *N*-heterocyclic carbenes, such as imidazol-2-ylidenes, which are regarded as ligands alternative to phosphanes. Those complexes are formed as a result of reactions of Pd complexes with imidazolium chloride salts representing a large group of ionic liquids (IL) [44]. As one of the first examples of such complexes, the bis-carbene Pd(II) complex (Scheme 11) [27] was used in the olefination of 4-bromoacetophenone with *n*-butylacrylate. At very low concentration (10^{-3} mol%), after activation with reducing agents like hydrazine or sodium formate, this carbene complex exhibited a high efficiency in the Heck reaction [27]. The same Pd(II) carbene complex used as the catalyst precursor in the Heck reaction of 4-chlorobenzaldehyde in the presence of [^{n}Bu$_4$N]Br reacts without induction time, which has been explained by the reducing action of some components of the catalytic system [27].

A palladium complex (Scheme 12(a)) with one halogen ligand (chloride) and a methyl group demonstrated high catalytic activity, and the Heck reaction started without an induction period [45]. Based on this observation, a mechanism has been proposed involving Pd(II) to Pd(0) reduction and the formation of a Pd(0) bis-carbene complex (Scheme 12(b)) [45]. According to that scheme, a Pd(0) complex may be formed by olefin insertion into the Pd–CH$_3$ bond, followed by β-hydride elimination and reductive elimination in the presence of a base (NaOAc) [45]. A 14-electron dicarbene species has been proposed as the reactive form in the Heck reaction catalyzed with Pd(Me)(carbene)$_2$Cl (carbene = 1,3-di-methylimidazol-2-ylidene) as the precursor [77].

Pd complexes with pyridine or carbonyl donors containing carbene ligands show high activity and stability in the Heck, Suzuki and Sonogashira coupling reactions [46]. The



Scheme 12. The mechanism of bis-carbene Pd(II) complex (a) and reduction to bis-carbene Pd(0) complex (b) [45].

importance of *N*-heterocyclic carbene palladium complexes in C–C coupling reactions have been reported [46]. Highly efficient, recyclable Pd(II) catalysts obtained in the reaction of Pd(cod)Cl(Me) with bis-imidazole ligands were used in the Heck reaction [47]. The stability of these complexes under reaction conditions was not discussed [47]. Bis-carbene pincer complexes of Pd(II) immobilized on K-10 montmorillonite catalyzed Heck coupling of phenyl halides with styrene [48].

2.4. Pd colloids as catalysts of Heck and carbonylation reactions

Metal colloids, usually regarded as nano-objects of 2–100 nm in size, have recently received increasing interest from many research groups which have applied metal nanoparticles in catalytic reactions [49–52]. Their high surface-to-volume ratios facilitate better access of substrates to the catalytically active metal centers compared with typical heterogeneous catalysts. This makes metal colloids very good candidates for active catalysts; however, their thermodynamic instability complicates practical applications [53].

Different synthetic routes for the preparation of Pd(0) colloids have been well known for many years. Among the many methods described in the literature, the reduction of Pd(II) to Pd(0) can be realized electrochemically [54] or chemically with the application of various reducing agents [53,55]. It has been found recently that $Pd(OAc)_2$ undergoes spontaneous reduction to colloidal nanoparticles under Heck reaction conditions when ethylacrylate reacts with iodobenzene in the presence of $[^{n}Bu_4N]Br$ and NaOAc [56]. Under Heck reaction conditions palladium nanoparticles are also formed from $PdCl_2(C_6H_5CN)_2$ upon reduction with acetate ion (Eqs. (2a) and (2b)). It was assumed that $PdCl_2(C_6H_5CN)_2$ reacted first with Na(OAc) to form $Pd(OAc)_2$ which undergoes decomposition with the formation of “palladium black”, methane, ethane, and CO_2 [56]:

$$PdCl_2(C_6H_5CN)_2/DMG \xrightarrow[130\,^{\circ}C]{Na(OAc)} Pd(0)\ colloid$$

$$(DMG = dimethylglycine) \tag{2a}$$

$$Pd(NO_3)_2 + (n\text{-}C_8H_{17})_4N^{+}(RCO_2)^{-} \xrightarrow[reflux]{THF} Pd(0)\ colloid \tag{2b}$$

When $Pd(OAc)_2$ was warmed-up in the presence of stabilizing agents like propylene carbonate or NMP (NMP = *N*-methylpyrrolidinone), it was possible to obtain a Pd(0) colloid stable for several days without noticeable agglomeration [58].

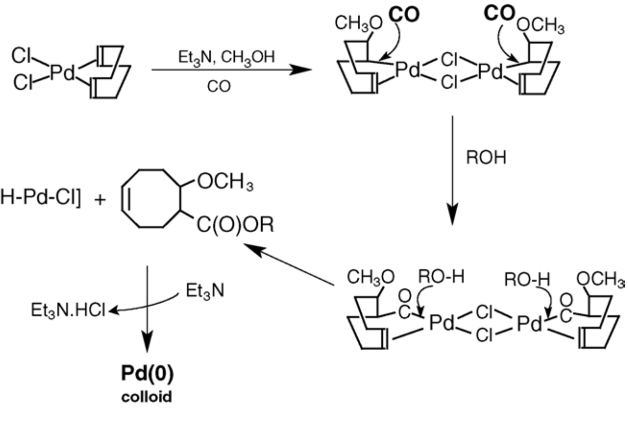
Pd(0) nanoparticles of 2–6 nm formed in a warmed-up solution of a palladium complex with benzothiazole carbenes in a mixture of TBAA (tetrabutylammonium acetate) and TBAB (tetrabutylammonium bromide) presented high stereospecificity in the Heck reaction of aryl bromides with 1,1-disubstituted olefins (butyl methacrylate and α-methylstyrene) as well as that of cinnamates with aryl halides [38]. In such reaction conditions Pd(0) nanoparticles formed from $Pd(OAc)_2$ were also catalytically active [38].

It has been proven experimentally that $Pd(OAc)_2$, $PdCl_2$, or $Pd(NO_3)_2$, catalyst precursors in the Heck coupling reactions, form Pd(0) nanoparticles during warming in THF in the presence of an excess of tetraalkylammonium carboxylates, $[R_4N]^{+}[RCO_2]^{-}$, which act as a reducing and stabilizing agents [57]. A Pd(0) colloid stabilized in the fluorous phase (1,5-bis(4,4′-bis(perfluorooctyl))phenyl-1,4-pentadien-3-one) has been obtained through $PdCl_2$ reduction with NaOAc in methanol and then used in the Heck and Suzuki reactions demonstrating high catalytic activity in several catalytic cycles [59].

In all the examples mentioned above, the Pd(0) nanoparticles which were formed in the presence of carboxylate anions, were regarded as reducing agents.

Another, rather rare, case of Pd(0) nanoparticles formation in a system not only free of phosphorus ligands but also of carboxylate ions as potential reducing agents is the reduction of $PdCl_2$(cod) to colloidal Pd(0) under carbonylation reaction conditions [43] (Scheme 13).

According to the reaction pattern presented in Scheme 13, the reduction of Pd(II) proceeds via the intermediate complex di-μ-chloro-bis(2-methoxycyclooct-5-ene)dipalladium(II), which is reduced by NEt_3 in the presence of CO and methanol. The above reduction mechanism has been proven by analytic determination of 2-alkoxy-5-cyclooctene carboxylic esters, also in experiments with deuterated alcohols [43]. XRD studies of the reaction mixture have revealed the presence of Pd(0) nanoparticles of 2.6–5.6 nm in size, probably responsible for the catalytic activity of the system [43]. Palladium reduction according to Scheme 13 has been carried out in methanol in the presence of PVP and the Pd(0)/PVP colloid obtained has been tested in a model carbonylation reaction of iodobenzene in molten ammonium salts as reaction medium. The similar catalytic



Scheme 13. The mechanism of $PdCl_2$(cod) reduction into Pd(0) colloid [43].

Table 1
Results of iodobenzene carbonylation with $PdCl_2$(cod) and Pd(0)/PVP colloid in CH_3OH with the addition of ammonium salts [$^n Bu_4N$]X type [43]

X (in [$^n Bu_4N$]X)	Catalyst precursor			
	$PdCl_2$(cod)		Pd(0)/PVP colloid[a]	
	Yield (%)	TON	Yield (%)	TON
–	17	31	4	16
Br	98	180	73	292
I	87	160	39	156
Cl	83	152	72	288
BF_4	95	174	70	280
PF_6	77	141	60	240

Reaction conditions: $[Pd] = 4.9 \times 10^{-5}$ mol.

[a] $[Pd] = 2.25 \times 10^{-5}$ mol, $[NEt_3] = 2.2 \times 10^{-2}$ mol, $[CH_3OH] = 2.5 \times 10^{-2}$ mol, $[PhI] = 9 \times 10^{-3}$ mol, $[^n Bu_4N]X = 9 \times 10^{-3}$ mol; 2 h, 5 atm CO, 70 °C.

activity of $PdCl_2$(cod) and the Pd/PVP colloid warrants the assumption that the reactive form of the catalyst in both cases is the same and originates from the palladium colloid (Table 1).

Identification of Pd(0) colloids in catalytically active systems obtained from different palladium precursors makes it possible to propose a new interpretation of phosphine-free systems in which the appearance of nanoparticles is consistent with the demonstrated catalytic activity. However, it is not definitely certain if soluble palladium colloids are true catalysts or just only the source of Pd(0) species which play an important role in catalysis.

Because of their thermodynamic instability, the catalytic activity of Pd(0) colloids strongly depends on reaction conditions and the presence of stabilizing agents to prevent nanoparticle agglomeration. Palladium concentration, or more precisely, palladium-to-substrate ratio, has also been found to be an important reaction parameter. In a Heck reaction catalyzed with Pd(0) nanoparticles formed from $Pd(OAc)_2$ the best yield of products is obtained at rather low concentrations of palladium, counteracting agglomeration [31,63].

The first experiments with a specially prepared Pd(0) colloid as the catalyst in the Heck reaction of unactivated aryl bromides gave a low yield of products [64,65]. Yields of up to 20% of the ester, only, were obtained in the carbonylation of benzyl bromide catalyzed by $PdCl_2$(cod) and in the carbonylation of iodobenzene catalyzed with a Pd(0) colloid obtained by reduction of $PdCl_2$(cod) and stabilized with PVP (Table 1) [43].

The catalytic activity of Pd(0) colloids, however, can be improved by the addition of ammonium salts, so-called Jeffery conditions, or by the use of ionic liquids as the reaction medium [60–62,88]. The beneficial effects exerted by ammonium salts on the Heck reaction were recently discussed [88].

A Pd(0) colloid prepared by reduction of the $[Pd(\eta^3\text{-allyl})_2Cl]_2$ precursor with Vcp_2 in the presence of PVP as a protecting polymer [66] has been found to be an active and stable catalyst of methoxycarbonylation of iodobenzene carried out in an ionic liquid (IL) as the reaction medium [67]. Under optimal reaction conditions, the yield of methoxycarbonylation catalyzed by the Pd(0) colloid depends on the kind of ionic liquid used and decreases in the order: [$^n Bu_4N$]Br (98%) > [$^n Bu_4N$]I (95%) > [$^n Bu_4N$]Cl (88%) > [bumepy]PF_6 (83%) > [Et_4N]Br (68%) > [bumepy]Cl (67%) > [bumepy]BF_4 (60%) > [Et_4N] Cl (38%) > [bmim]PF_6 (35%) > [bmim]BF_4 (18%) > [bmim] Cl (8%) [67]. Such an order can be related to the ability of the salts to stabilize the Pd(0) colloid during the catalytic process. Pyridinium type ionic liquids, of the [bumepy]X type (X = Cl, PF_6, BF_4), were much better than the imidazolium, [bmim]X type. When the Pd(0) colloid is used in a pyridinium salt medium, its catalytic activity is prevented and it can be recycled several times with only small loss of the activity (Fig. 1) [67]. In contrast, imidazolium salts strongly inhibit methoxycarbonylation, which may suggest the formation of catalytically inactive intermediates, for example palladium carbene complexes. The strong inhibiting effect of imidazolium chlorides and bromides has also been observed in other palladium-catalyzed carbonylation reactions [44].

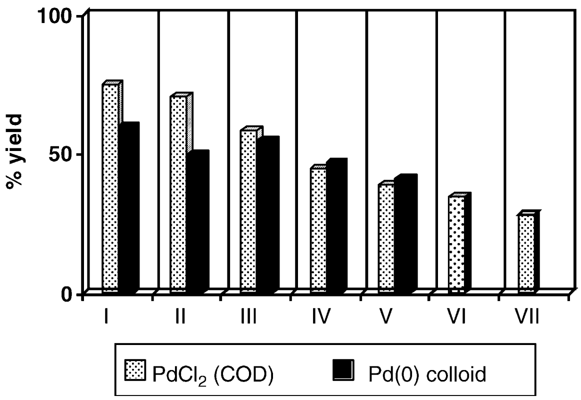
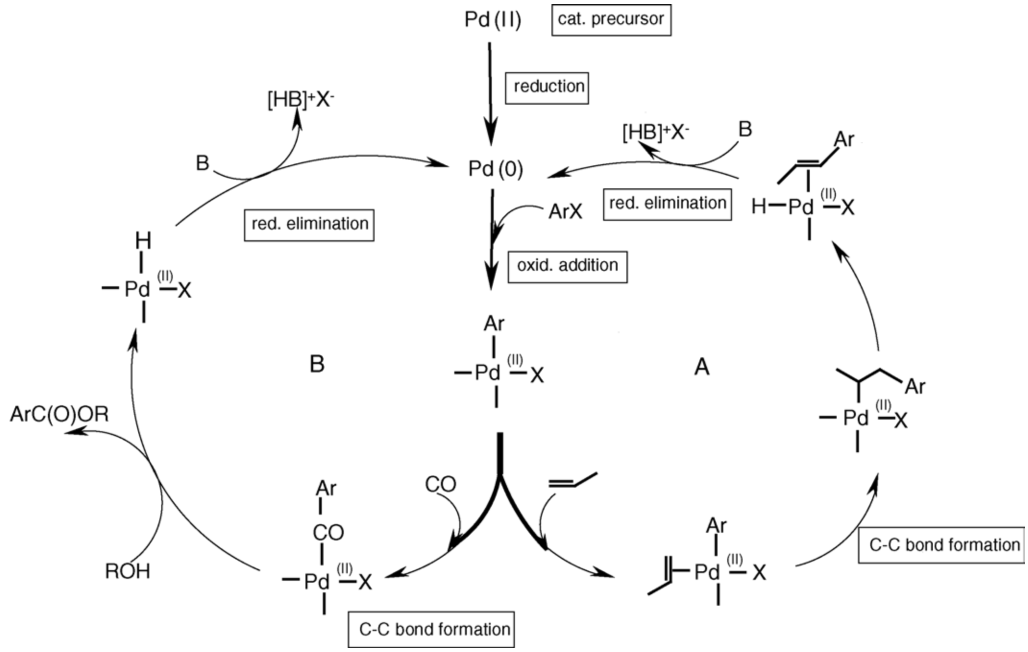


Fig. 1. Repetitive methoxycarbonylation of iodobenzene with $PdCl_2$(cod) and Pd(0)/PVP colloid in [bumepy]BF_4 (90 °C, 5 atm CO) [44,67].

3. The mechanisms of the Heck and carbonylation reactions

According to widely accepted knowledge, both Heck and carbonylation reactions are catalyzed by Pd(0) species, usually formed in situ from palladium(II) catalyst precursors in reaction with a reducing agent present in the system [1]. As a result of oxidative addition of aryl halide, the same substrate in both reactions, Pd(0) is converted into a Pd(II) species, an active intermediate (Scheme 14). Another version of the Heck reaction mechanism, involving the Pd(II)/Pd(IV) redox couple instead of Pd(0)/Pd(II), is also presented in some papers. That rather unusual mechanism can be supported by the isolation of a Pd(IV) complex [33]. However, the results presented and discussed above prompt us

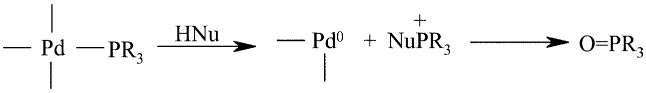


Scheme 14. Combined mechanism of Heck (A) and carbonylation (B) reactions.

to prefer the mechanism with the Pd(II)/Pd(0) redox system (Scheme 14).

3.1. Pd(II) reduction to Pd(0)

Reduction of Pd(II) to Pd(0) is the first step in generally accepted in both Heck and carbonylation reaction mechanisms [1,4,68,69]. The reduction of Pd(II) to Pd(0) assisted by hard nucleophiles, such as OH^-, F^-, or OR^-, has been studied in detail, and a general scheme of this reaction has been proposed (Eq. (3)) [4]:



$$-Pd-PR_3 \xrightarrow{HNu} -Pd^0 + \overset{+}{Nu}PR_3 \longrightarrow O{=}PR_3 \quad (3)$$

Studies on palladium reduction by a hydroxide ion have shown the importance of OH^- attack on coordinated PPh_3, followed by oxygen transfer and $OPPh_3$ formation [70]. Similarly, the mechanism proposed for reduction by F^- was supported by the observation of PPh_3F_2 in the reaction medium (Eq. (4)) [71]:

$$PdCl_2(PR_3)_2 \xrightarrow[PR_3]{F^-,H_2O} Pd(PR_3)_4 + O{=}PPh_3 \quad (4)$$

The reduction of Pd(II) in the $Pd(OAc)_2(PPh_3)_2$ complex has been the subject of thorough studies that have revealed spontaneous reduction accompanied by the formation of a Pd(0) complex of the formula $[Pd^0(PPh_3)_3(OAc)]^-$ [72,73]. The reaction proceeds via an intramolecular reduction in which PPh_3 reduces Pd(II) via an inner sphere atom transfer, and phosphine is oxidized to phosphine oxide (Eq. (5)) [72,73]:

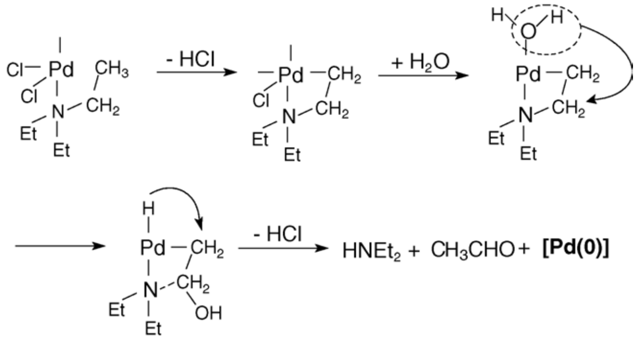
$$Pd(OAc)_2 + 3PPh_3 + H_2O \rightarrow Pd^0(PPh_3)_2(OAc)^- + O{=}PPh_3 + AcOH + H^+ \quad (5)$$

Other Pd(II) complexes with oxygenated ligands, such as $NO_3{}^-$, $CF_3CO_2{}^-$, acac$^-$, or OH^-, react with phosphine in the same way [72].

The reaction of NEt_3 with $PdCl_2(PPh_3)_2$ was reported already in 1973, and it has been known since then that *tertiary* amines, in contrast to secondary amines, do not reduce palladium in the $PdCl_2(PPh_3)_2$ complex [74]. The reaction of $PdCl_2(PPh_3)_2$ with CO in methanol in the presence of NEt_3 leads to the formation of the stable carbomethoxy Pd(II) complex $Pd(COOMe)(Cl)(PPh_3)_2$ [74]. The formation of palladium metal has, however, been reported in a system containing $PdCl_2(PPh_3)_2$, NEt_3, and water [70].

The reaction of $PdCl_2(P(OPh)_3)_2$ with NEt_3 or with other amines, like NPr_3 or NBu_3, in the presence of water proceeds in a different way, and the final product is the $Pd[P(OPh)_3]_4$ complex [75,76]. Simultaneously, amines undergo decomposition to corresponding aldehydes and secondary amines. The proposed mechanism of this reaction is shown in Scheme 15. The reaction starts with the activation of the C–H bond of the amine coordinated to palladium, and the next step consists in nucleophilic attack of OH^- from water on the α-carbon of the intermediate complex. The rearrangement in the coordination sphere of palladium is connected with electron transfer leading to the formation of aldehyde and secondary amine (Scheme 15) [76].

The very special role of amines and water in the Pd(II) reduction mechanism presented above has been explained and proven in experiments with deuterated reagents. The results



Scheme 15. The mechanism of Pd(II) reduction by NEt_3 at the presence of H_2O [76].

show that two protons in the acetaldehyde formed originate respectively from H_2O and NEt_3 molecules (Scheme 16).

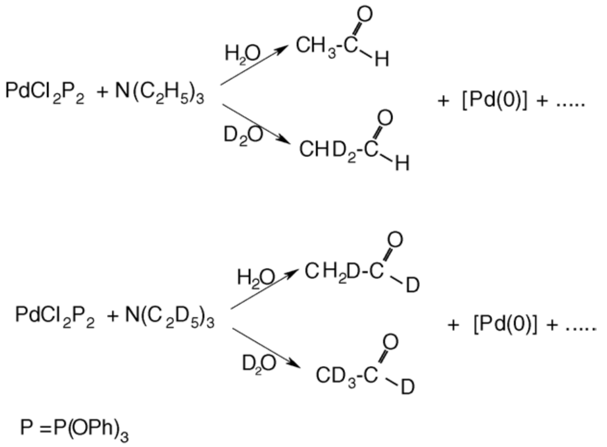
3.2. *Oxidative addition of aryl halides to Pd(0) complexes*

As has been shown, the key stage in the Heck reaction as well as in the carbonylation reaction is the activation of the substrate, aryl halide, via oxidative addition to Pd(0). There is a considerable amount of experimental evidence for the structures of the aryl and benzyl complexes formed in this reaction (Eq. (6))

$$[\mathrm{Pd(0)}] + \mathrm{PhX\,(or\,PhCH_2X)} \rightarrow [\mathrm{XPd(II)(Ph)(or\,CH_2Ph)}] \quad (6)$$

In reactions of aryl halides, PhBr and PhI, with $Pd(PPh_3)_4$, *trans*-$[Pd(Ph)(PPh_3)_2X]$ (X = Br, I) complexes were obtained, and then complexes with X = F and Cl were also synthesized via halogen exchange [68,78,79]. The thermal stability and decomposition paths of these complexes were studied [80]. The oxidative addition of aryl halides to Pd[P(*o*-tol)$_3$]$_2$ at room temperature leads to dimeric products of *trans*-{Pd[P(*o*-tol)$_3$](Ph)(X)}$_2$, where X = Br, I; Ph = *p*-MeC$_6$H$_4$, *p*-^{n}BuC$_6$H$_4$, *p*-^{t}BuC$_6$H$_4$ [81,82]. The reaction of $Pd(dba)_2$ (dba = dibenzylidene acetone) with excess (*p*-^{t}BuC$_6$H$_4$)Br and dioxolane P-, O-type ligands leads to oxidative addition products [83]. In situ formation of a dimeric aryl complex has been observed in the presence of the hydroxide ion, which is responsible for the generation of a Pd(0) species from $PdCl_2(PPh_3)_2$ (Eq. (7)) [70]:

$$2PdCl_2(PPh_3)_2 + 2PhI + 6KOH \rightarrow [PPh_3Pd(Ph)(\mu\text{-}OH)]_2 + 2OPPh_3 + 2KI + 4KCl + 2H_2O \quad \text{(benzene–}H_2O\text{, reflux for 3–5 h)} \quad (7)$$



Scheme 16. Deuterium distribution in the reaction of $PdCl_2(P(OPh)_3)_2$ with NEt_3 and H_2O or D_2O [76].

Dimeric aryl and benzyl complexes of the type $[Pd_2(\mu\text{-}Cl)_2R_2P_2]$ have been obtained in the reaction of $Pd_2(\mu\text{-}Cl)_2Cl_2P_2$ ($P = PPh_3$, $PMePh_2$, PBu_3) with diorganomercurials R_2Hg [84]. A mononuclear complex, *trans*-(η^1-CH$_2$Ph)Pd(Br)(PPh$_3$)$_2$, has been synthesized as a product of oxidative addition of $PhCH_2Br$ to $Pd(PPh_3)_4$ [85a]. The reactions of diphosphine arylpalladium species with styrene have been studied with respect to the regioselectivity of the coupling products formed [85b]. The (bromo)styrylpalladium(II) complex was prepared by oxidative addition of PhCH=CHBr to $Pd(PPh_3)_4$ [85c]. Oxidative addition products have also been obtained for Pd(0) bis-*N*-heterocyclic carbene complexes postulated as active intermediates in C–C coupling reactions [77]. The mono-carbene σ-aryl complex was derived by a different route, in the reaction of the aryl complex, $[Pd(Ph)(\mu\text{-}OH)(PPh_3)]_2$ with $[IprH]^+Cl$ (IprH = *N*,*N*′-bis(2,6-diisopropylphenyl)imidazolium cation) [86].

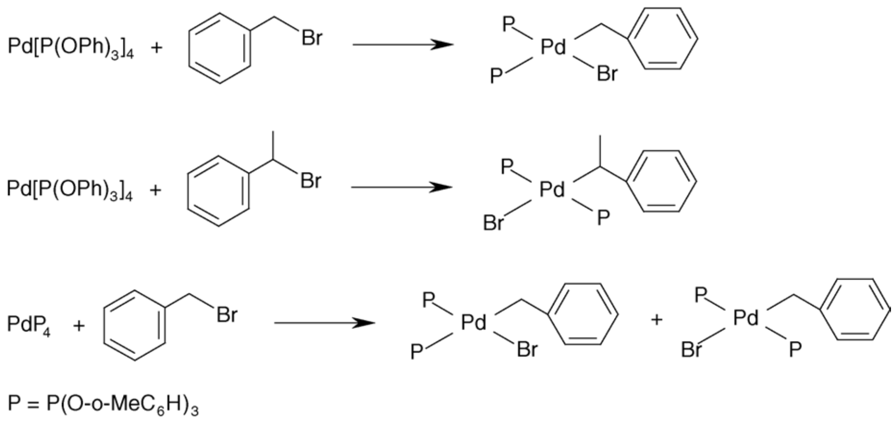
Fast reaction of the $Pd(PNS)_4$ complex with benzyl bromide was demonstrated by $^{31}P\{^1H\}$ NMR measurements [26]. Immediately after the addition of benzyl bromide to the solution of $Pd(PNS)_4$ in CD_3OD, a new intense signal at 29.4 ppm appeared besides the one at 16.7 ppm, assigned to the starting Pd(0) complex (Eq. (8)) [26]:

$$\underset{16.7\,\mathrm{ppm}}{Pd(PNS)_4} + PhCH_2Br \rightarrow \underset{29.4\,\mathrm{ppm}}{Pd(PNS)_2(PhCH_2)(Br)} \quad (8)$$

A similar chemical shift (27.9 ppm) was detected for the $Pd(Ph)Br(TPPTS)_2$ complex, isolated as a product of oxidative addition of bromobenzene to $Pd(TPTS)_3$ [18].

The $Pd[P(OPh)_3]_4$ complex, obtained by the reduction of $PdCl_2[P(OPh)_3]_2$ with $NaBH_4$, reacts with benzyl bromide forming a benzyl complex, *cis*-PdBr(CH$_2$Ph)[P(OPh)$_3$]$_2$, in a few minutes [14,75]. $^{31}P\{^1H\}$ NMR spectra and X-ray studies in the solid state confirmed the *cis* position of both the $P(OPh)_3$ ligands. The two Pd–P bonds are non-equivalent with the Pd–P bond *trans* to the benzyl ligand being markedly longer, pointing to a stronger *trans* influence of the benzyl ligand.

Although *cis* geometry is expected for the oxidative addition product, in most of the isolated stable complexes aryl (or benzyl) and halogen ligands occupy *trans* positions. By changing the steric requirements of phosphorus as well as aryl (benzyl) halides, it has been observed that steric



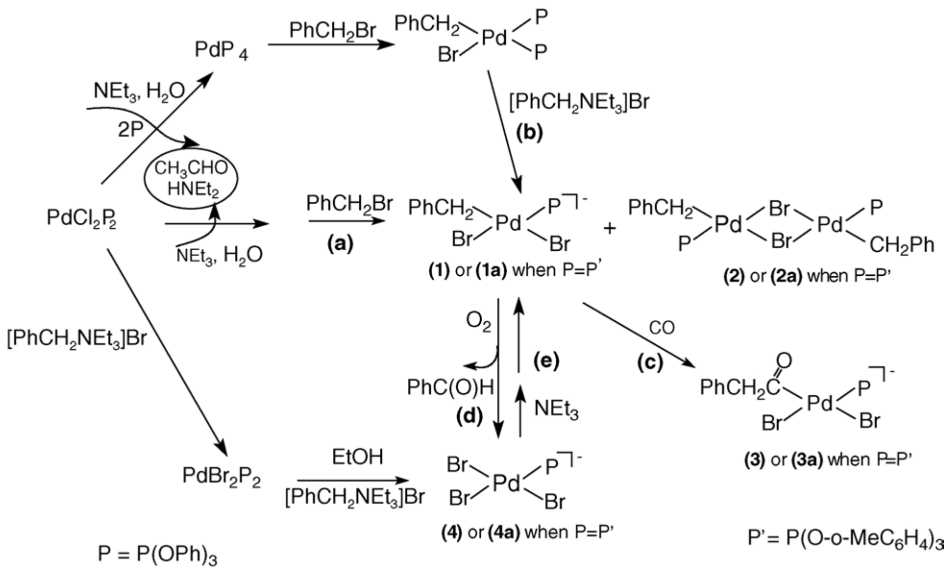
Scheme 17. Products of oxidative addition of benzyl bromides to Pd(0) complexes.

hindrance is decisive for the geometry of oxidative addition reaction products. When the Pd[P(O–*o*-MeC$_6$H$_4$)$_3$]$_4$ complex reacted with benzyl bromide, a mixture of *cis*- and *trans*-isomers of Pd(CH$_2$Ph)(Br)[P(O–*o*-MeC$_6$H$_4$)$_3$]$_2$ was obtained [14]. Oxidative addition of 1-bromoethylbenzene to Pd[P(OPh)$_3$]$_4$ was slower than that of benzyl bromide, and *trans*-PdBr(PhCH(Me))[P(OPh)$_3$]$_2$ was identified in solution the next day (Scheme 17).

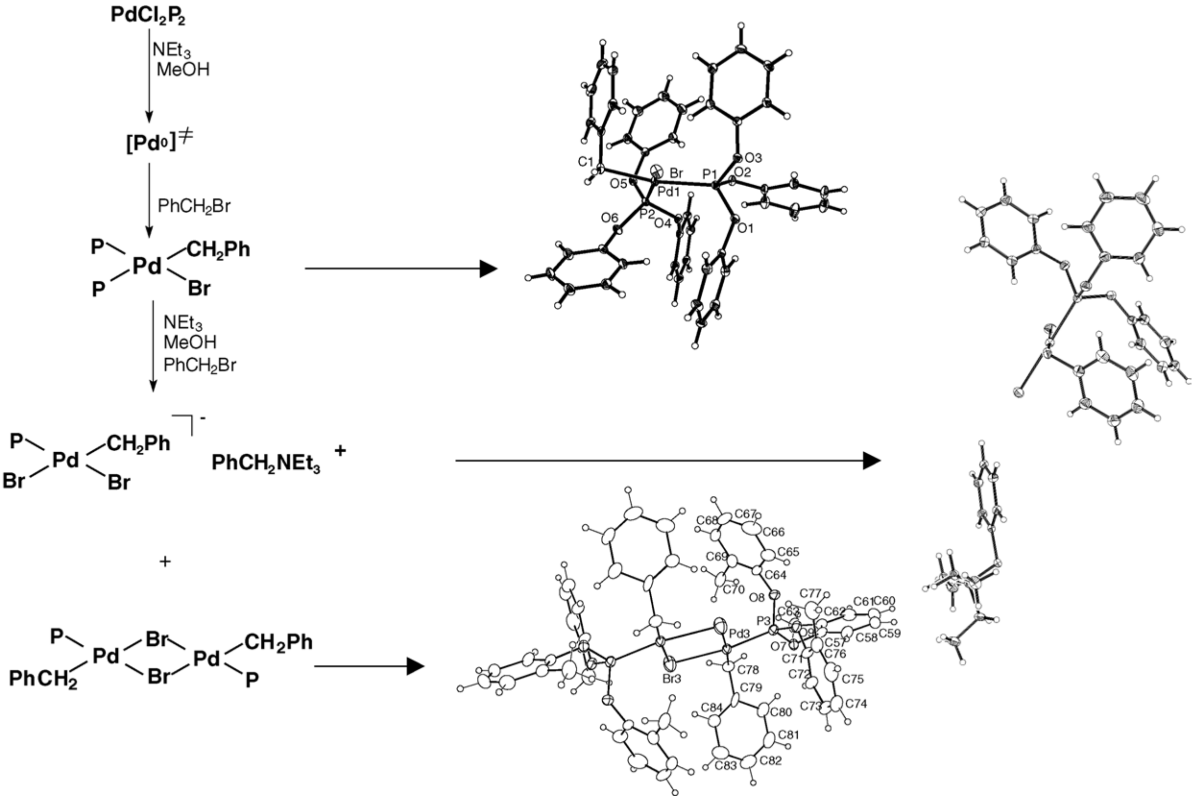
Following in situ reduction of PdCl$_2$[P(OPh)$_3$]$_2$ with NEt$_3$, with addition of PhCH$_2$Br, without separation of the Pd(0) species, the oxidative addition product *cis*-[PdBr$_2$(CH$_2$Ph)(P(OPh)$_3$)]-[PhCH$_2$NEt$_3$] was isolated and structurally determined (Scheme 18, route a) [76].

The same complex has also been obtained in the reaction of *cis*-PdBr(CH$_2$Ph)[P(OPh)$_3$]$_2$ with [PhCH$_2$NEt$_3$]Br (Scheme 18, route b, product **1**). In situ reduction with NEt$_3$ of a palladium complex containing a phosphite of higher steric hindrance, PdCl$_2$[P(O–*o*-MeC$_6$H$_4$)$_3$]$_2$, followed by oxidative addition of benzyl bromide made it possible to isolate a dimeric benzyl complex of the formula [PdBr(CH$_2$Ph)[P(O–*o*-MeC$_6$H$_4$)$_3$]$_2$ (Scheme 18, route b, product **2a**) [76]. The presence of intermediates containing benzyl ligands is very important for the activity of the catalytic system since its reaction with CO and MeOH leads directly to esters, the methoxycarbonylation reaction products (Scheme 19). The formation of acyl complexes (Scheme 18, route c, product **3**) in reactions of the benzyl complexes *cis*-[PdBr(CH$_2$Ph)(P(OPh)$_3$)]$_2$ and *cis*-[PdBr$_2$(CH$_2$Ph)(P(OPh)$_3$)][PhCH$_2$NEt$_3$] with CO was proven by IR spectra, showing ν(CO) frequencies at 1709 and 1700 cm^{-1}, respectively.

Attempts to synthesize the benzyl complex *cis*-[PdBr$_2$(CH$_2$Ph)(P(OPh)$_3$)][PhCH$_2$NEt$_3$] in the presence of air (Scheme 18, route d) failed, and an anionic complex structurally determined as [PdBr$_3$(P(OPh)$_3$)][PhCH$_2$NEt$_3$] (product **4**) was isolated instead [76]. Fortunately for its catalytic activity, this complex can be easily converted into a palladium benzyl complex,



Scheme 18. Reactions of PdCl$_2$P$_2$ complexes with PhCH$_2$Br leading to benzyl Pd(II) and related complexes.



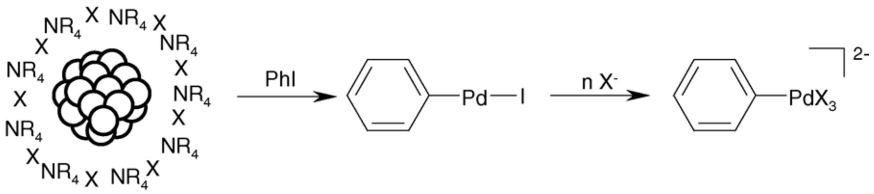
Scheme 19. Molecular structures of benzyl Pd(II) complexes.

cis-[$PdBr_2(CH_2Ph)(P(OPh)_3)$][$PhCH_2NEt_3$] (product **1**), by treatment with NEt_3 and then with benzyl bromide (Scheme 18, route d).

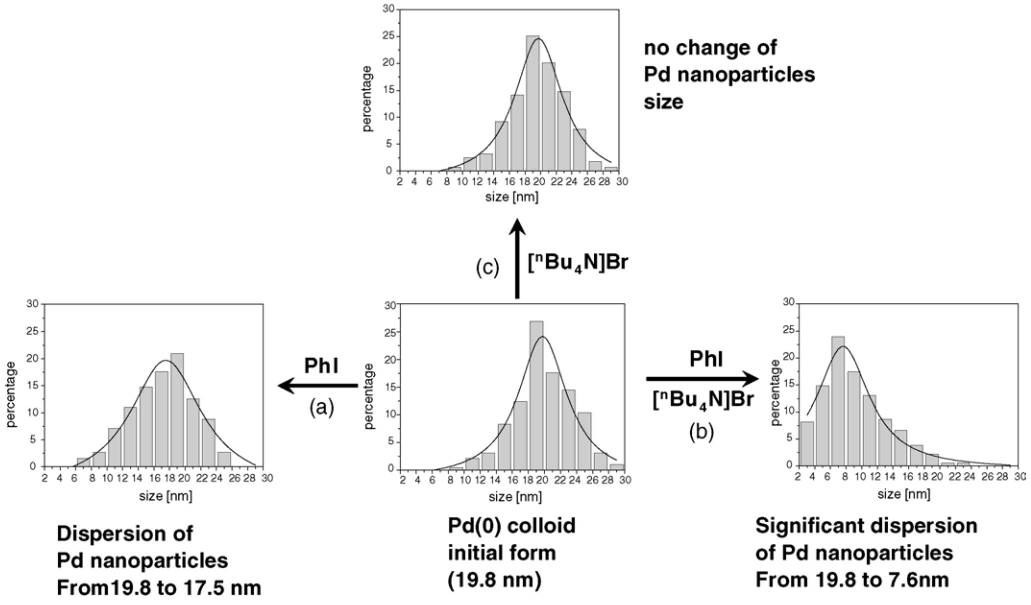
3.3. Oxidative addition of aryl halides to a Pd(0) colloid

The first example of oxidative addition of iodobenzene to a Pd(0) colloid stabilized with [$^nOct_4N$]$^+$[HCO_2^-] was reported by Reetz and Westermann [56]. When the reacting solution in NMP/THF was warming, a color change from black to dark red was observed followed by a decrease of UV–vis absorption in the 400–650 nm region characteristic of Pd(0) colloids. ^{13}C NMR measurements showed the appearance of new signals, which were assigned to the oxidative addition product, $Pd(Ph)X_3^-$ (anion X from an ammonium salt added for stabilization of the Pd(0) colloid) (Scheme 20) [56].

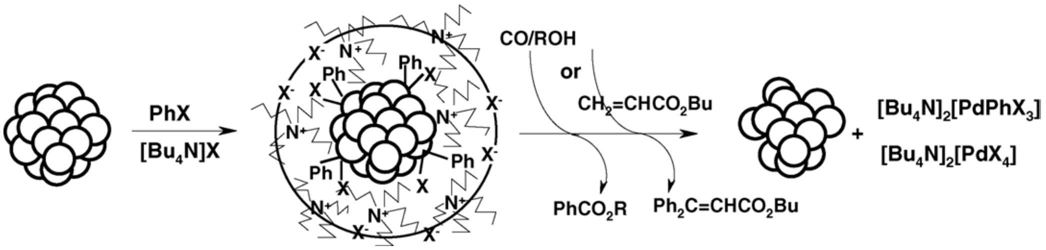
The formation of similar ionic species, analogous to those identified in phosphine-containing systems, has been proposed in several catalytic systems containing ammonium salts applied in the Heck reaction [38]. However, confirmation of those results was not possible until combined interpretation of TEM (transmission electron microscopy) and XPS (X-ray photoelectron spectroscopy) measurements had been performed for samples taken directly from the reaction mixture [87]. A Pd(0) colloid containing nanoparticles of relatively large size (19.8 nm) was used for reactions with PhI (Scheme 21, route a). As a result, insignificant dispersion (from 19.8 to 17.3 nm) was observed. However, when the same reaction with PhI was conducted in the presence of [$^nBu_4N$]Br (Scheme 21, route b), the dispersion of Pd(0) nanoparticles was much more significant: from 19.8 to 7.6 nm. The Pd(0) colloid treated with [$^nBu_4N$]Br only (Scheme 21, route c) remains practically unchanged. The reaction of the Pd(0) colloid with PhBr in the presence of [$^nBu_4N$]I also led to significant nanoparticle dispersion, from 19.8 to 11.7 nm [87].



Scheme 20. Oxidative addition of PhI to Pd(0) colloid [56].



Scheme 21. Pd(0) nanoparticles size distribution [87].



Scheme 22. Proposed transformations of Pd(0) colloid at the presence of PhX and $[^n\mathrm{Bu_4N}]$X into soluble Pd(II) complexes.

The experiments described above, have provided evidence for cooperative interactions of Pd(0) nanoparticles with aryl halides and ammonium salts. The products of these reactions were identified using the XPS method. A simple experiment involving XPS-monitored interactions of PhI or PhBr with a Pd(0) colloid revealed the appearance of Pd(II) on the surface of the Pd(0) colloid as a result of the oxidative addition reaction. The participation of ammonium salts in the oxidative addition of aryl halides to the Pd(0) colloid led to ionic species of the formula $[^n\mathrm{Bu_4N}]_2[\mathrm{PdPhX_3}]$ and/or $[\mathrm{Bu_4N}]_2[\mathrm{PdX_4}]$. Similar forms have also been proposed by Reetz and Westermann (Scheme 20) [56]. The ionic Pd(II) complexes, which are soluble in the reaction medium, may leave the colloid surface, leading to a decrease in the Pd(0) nanoparticle size (Scheme 22). Under real Heck or carbonylation reaction conditions, one may expect the existence of some kind of equilibrium between nanosize colloidal Pd(0) and monomolecular Pd(0) complexes, both soluble and catalytically active (Schemes 3 and 22). Ammonium salts not only stabilize the nanoparticle but also facilitate solubilization of the catalytic system components, which form soluble Pd(II) complexes of the general formula $[\mathrm{R_4N}]_2[\mathrm{PdPh}_m\mathrm{X}_n]$ $(n+m=4)$. During the catalytic reaction these species can undergo reduction with the formation of nanoparticles of a different size than in the starting Pd(0) colloid.

4. Conclusions

- While not complete, the review of papers dealing with aryl halide carbonylation and Heck reactions is sufficient to provide arguments supporting the view that both monomolecular Pd(0) phosphine complexes and nanosized Pd(0) colloids can act as active catalysts.
- It is possible that the typical monomolecular Pd(0) complexes (e.g. $[\mathrm{Pd(0)P_4}]$, P = phosphorus ligand) will undergo partial decomposition during the catalytic process to form nanosized phosphine-free Pd(0) particles.
- Palladium in the form of a colloid is a good catalyst for Heck and carbonylation reactions, especially when applied in an ammonium salt ($[\mathrm{R_4N}]$X) or an ionic liquid (IL) medium. Ammonium salts efficiently contribute to the formation of soluble, monomolecular Pd(0) compounds of probably higher catalytic activity than bigger-sized clusters.

- Carboxylate salts, frequently used as bases in the Heck reactions, can act as effective Pd(II) to Pd(0) reducing agents, and therefore they also may initiate the formation of colloidal nanoparticles.
- Recent studies have provided arguments for the existence of an important equilibrium between monomolecular Pd(0) species and nanosized Pd(0) colloids in real ligand-free catalytic systems. However, further studies are needed to confirm the existence of similar equilibriums in phosphine-containing systems (Scheme 3).

Acknowledgements

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