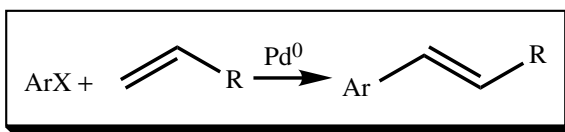


PART IV

Palladium-Catalyzed Reactions Involving Carbopalladation



IV.1 Background for Part IV

STEFAN BRÄSE and ARMIN DE MEIJERE

A. INTRODUCTION

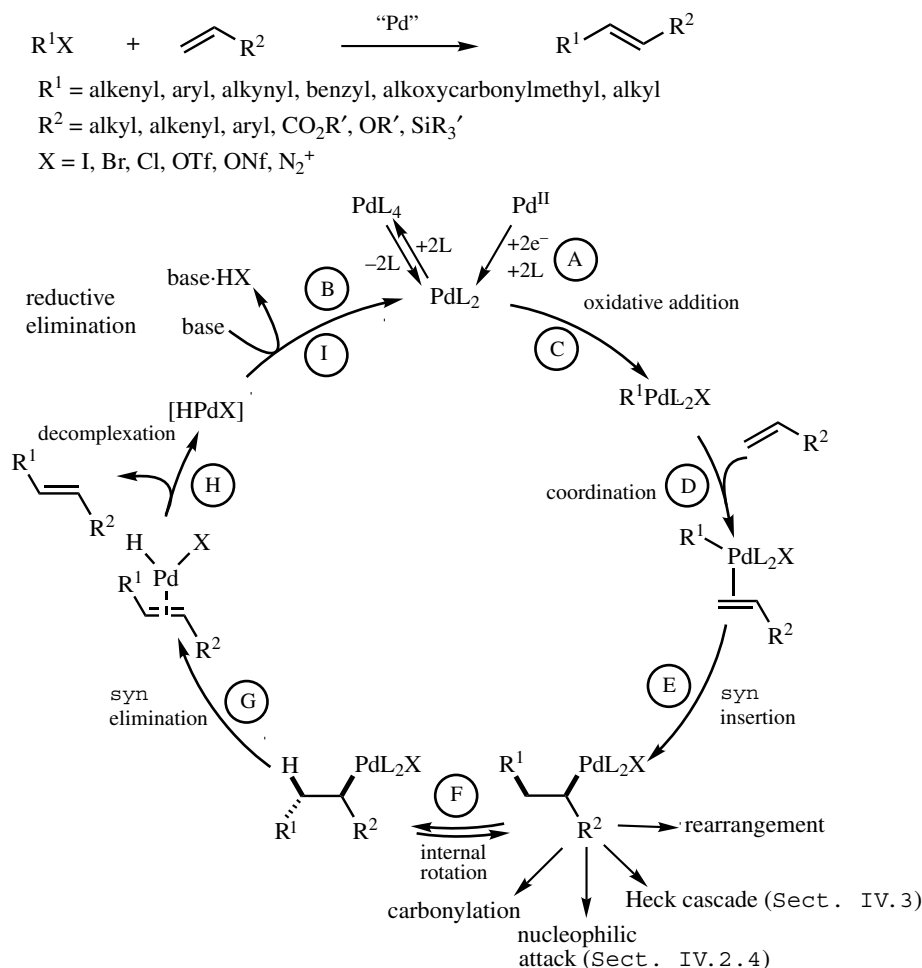
Around 1970, Mizoroki et al.^[1] and Heck and Nolley^[2] independently designed and executed the first Pd-catalyzed coupling reactions of aryl and alkenyl halides with alkenes.^{[3]–[7]} In subsequent investigations Dieck and Heck demonstrated the usefulness and rather broad scope of this new catalytic transformation. The real drive to utilize this powerful C—C bond-forming process, however, began only in the second half of the 1980s, and by now an impressive number of publications have established the so-called Heck reaction as an indispensable method in organic synthesis. Alkynylations of aryl and alkenyl halides, frequently also considered as Heck reactions, are described in **Sect. III.2.8**. Although Dieck and Heck were among the first investigators of this reaction,^[8] the drastically improved conditions applying copper salts as cocatalysts were developed by other groups (cf. **Sect. III.2.8.1**). Applications of the Heck reaction range from the preparation of a large variety of hydrocarbons, novel polymers, and dyes to advanced strategies for enantioselective syntheses of natural products. The simultaneous developments of mechanistically related variants, namely, the Sonogashira, Suzuki, Stille, and Negishi coupling reactions (**Sects. III.2.8, III.2.2, III.2.3, and III.2.1** in this volume, respectively) of alkenyl- and arylmetal derivatives with alkenes and the metal-catalyzed formation and cycloisomerization of enynes have profited from the improvement of and mechanistic insights into carbometallation reactions in general. The converse, of course, applies as well. Using only a catalytic amount of a palladium(0) complex, cross-couplings like the Heck reaction involving carbometallation steps can bring about structural changes with unprecedented increases in structural complexity, particularly when conducted as intramolecular reaction cascades. Although the potential of this Pd-catalyzed process has not yet been fully explored, it is appropriate to say, even at this stage, that carbometallation reactions are true “power tools” in contemporary organic synthesis.

B. MECHANISM

Even the early concepts concerning the mechanism of the Heck reaction served as reasonable working hypotheses (for details see **Sect. IV.2.1.1**). The actual C—C bond-forming reaction is a carbopalladation of C,C double bond, and it can be used to bind alkenyl, aryl, allyl (the intramolecular carbometallation of an allylic substrate is called a

palladaene reaction^{[9]–[11]}), benzyl, methyl, alkoxycarbonylmethyl, alkynyl,^[12] certain alkyl,^[13] and silyl fragments to a variety of alkenes. In terms of the involved mechanisms, all of these cross-couplings may be considered as Heck reactions. The leaving groups on the coupling partners can be halides, sulfonates, nitrogen (diazonium salts as substrates), and a variety of other groups, which are less commonly employed. For a discussion and summary, see **Sect. D**.

A coordinatively unsaturated 14-electron palladium(0) complex, usually containing two tertiary phosphanes as weakly electron-donating ligands, has been proved to be the catalytically active species. It is commonly generated *in situ* from either from a palladium(0) complex or by reduction of relatively inexpensive palladium(II) acetate or chloride.^{[14]–[18]} In the first step of the catalytic cycle (© in **Scheme 1**), a haloalkene, a haloarene, or a similar substrate is oxidatively added to the coordinatively unsaturated palladium(0) species to generate a σ -alkenyl- or σ -arylpalladium(II) complex.^{[19]–[21]} This then coordinates an alkene molecule, and when the latter and the alkenyl (aryl) residue on the palladium are in a *cis* orientation, the σ -alkenyl- or σ -arylpalladium complex can



undergo *syn* insertion into the C,C double bond of the in-plane coordinated alkene, to yield a σ -(β -alkenyl)- or σ -(β -aryl)alkylpalladium halide complex. The product-yielding β -hydride elimination step (Ⓢ in **Scheme 1**) can occur only after an internal rotation (step Ⓣ) around the former double bond, as it requires a β -hydrogen atom to be oriented *syn-planar* with respect to the halopalladium residue. The subsequent *syn* elimination of a hydridopalladium halide—examples of *anti* elimination are also known^[22]—to yield an alkene, is reversible, and therefore the thermodynamically more stable 1,2-disubstituted (*E*)-alkene is generally obtained when the coupling is performed with a terminal alkene. Reductive elimination of HX from the hydridopalladium halide, aided by the added base, regenerates the active catalyst and thereby (step Ⓚ) completes the catalytic cycle.

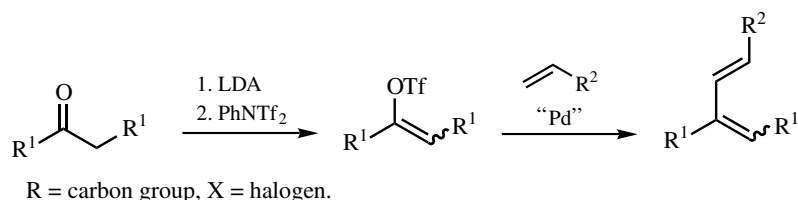
This mechanism has not been proved in every detail, and especially the rate-determining step has not been identified unequivocally in all cases. For many substrates the oxidative addition can rightly be assumed to be rate-determining; however especially in the coupling of tetrasubstituted alkenes, the oxidative addition most probably is not rate determining (**Sect. IV.2.1.1**).

C. SYSTEMATIC CLASSIFICATION OF CARBOPALLADATIONS

The carbometallation of π -compounds can proceed by various modes.

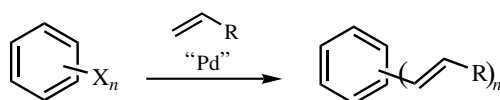
C.i. Carbopalladation with C—Pd Single Bonds

C.i.a. Four-Centered Processes. The carbopalladation of a C,C multiple bond with a carbon–palladium single bonds is the key step in the catalytic cycle of the standard Heck reaction, the intermolecular version of which has been used extensively since its discovery for the functionalization and derivatization of aryl and alkenyl halides,^[6] as well as alkenyl triflates or the more reactive nonaflates,^[23] which are readily available from the corresponding ketones (**Scheme 2**) (**Sect. IV.2.1.2**).



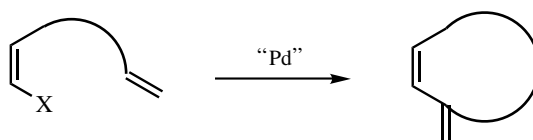
Scheme 2

Multifold Pd-catalyzed cross-coupling reactions on oligohaloalkenes and -arenes can most elegantly and easily lead to highly substituted carbo- and heterocyclic systems. Up to a sixfold Heck coupling, with the formation of mixtures of isomers, however, has been reported^[24] ($n = 6$, X = Br, **Scheme 3**) (**Sect. IV.2.1.2**).



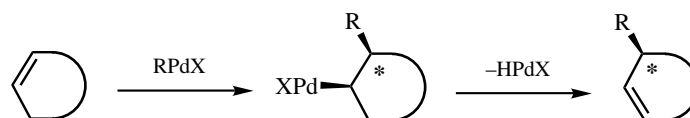
Scheme 3

The intramolecular Heck reaction provides a general access to carbocyclic (**Sect. IV.2.2.1**) and heterocyclic (**Sect. IV.2.2.2**) systems. All ring sizes from three- to nine-membered and even larger rings are achievable. However, certain restrictions apply in those cases in which rings smaller than six-membered are formed; that is, these rings are accessible only by *n-exo* processes (**Scheme 4**).



Scheme 4

Asymmetric synthesis has become the most relevant access to enantiomerically pure compounds, and transition-metal-induced reactions are increasingly important in the array of methods for the enantioselective construction of new asymmetric centers. Catalytic processes, in which chiral information is transferred from a small fraction of a chiral auxiliary in the catalyst to a large fraction of the prochiral substrate, are rapidly developing into extremely valuable methods. Among the established methods, however, are only a few for the catalytic enantioselective formation of carbon–carbon bonds. An ordinary Heck reaction, that is, the coupling of an aryl or alkenyl derivative with an alkene, does not form a new center of chirality. With cyclic alkenes, however, the stereoselective *syn*- β -hydride elimination after the *syn*-addition of the organylpalladium species can only occur in such a way that a nonconjugated diene is formed.^[25] With chiral ligands on the palladium catalyst, the new stereogenic center can be generated in an enantioselective way.^[26] (**Scheme 5**).



Scheme 5

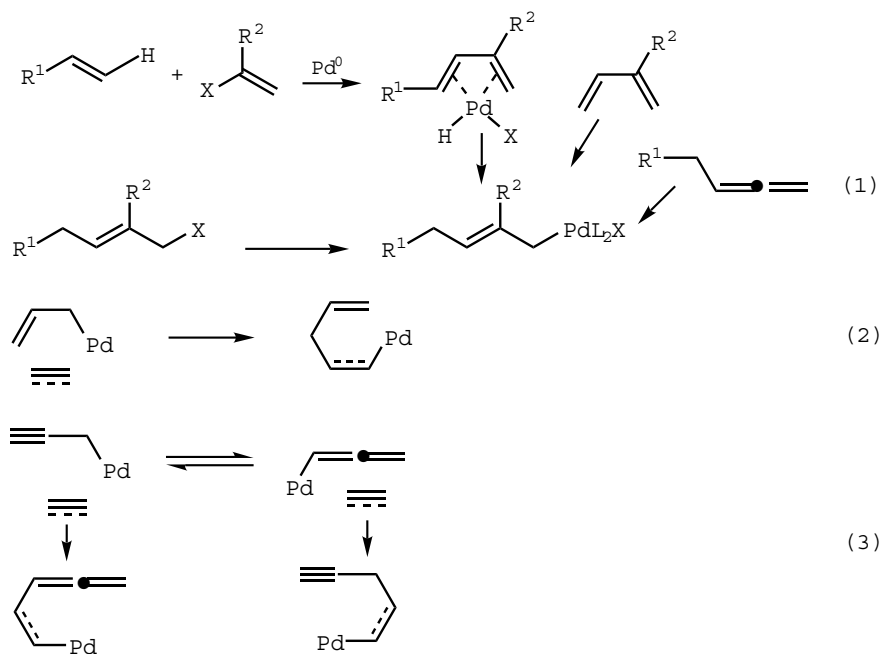
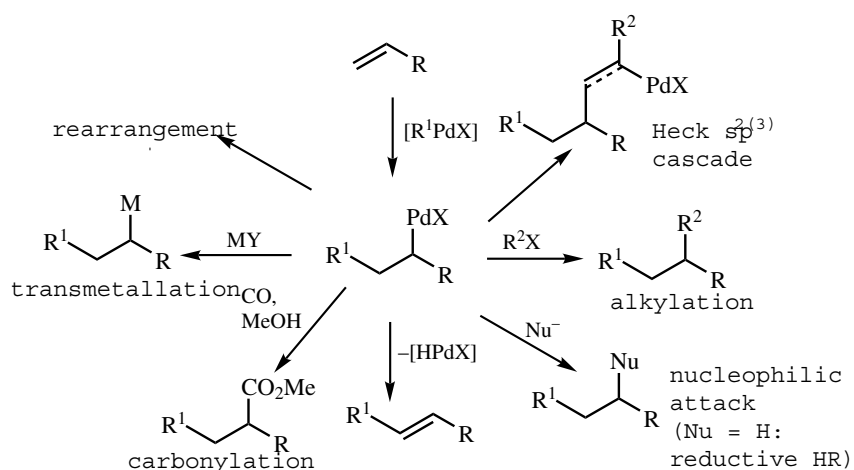
While neopentyl-type and related σ -alkylpalladium complexes are stable toward dehydropalladation, all ordinary alkylpalladium complexes formed by carbopalladation of alkenes do undergo β -hydride elimination more or less rapidly. However, under certain structural preconditions and also, to a certain extent, controlled by the external conditions, rearrangements, further carbopalladations (**Sect. IV.3**), transmetalations, carbonylations, or nucleophilic substitutions (e.g., by hydride) can occur prior to β -dehydropalladation.

Cascade reactions arising from sequential carbopalladations are especially valuable for the construction of various carbo- and heterooligocyclic systems with three, four, or even more annelated rings. The Heck reaction has successfully been employed in various inter–inter-, intra–inter-, as well as all–intramolecular reaction cascades (**Sect. IV.3**). In the carbopalladation step of the Heck reaction (**Scheme 6**) a new metal–carbon bond is formed, which, in principle, can undergo any of the typical reactions of a σ -M–C bond, when the β -hydride elimination is not too fast. When the β -hydride elimination is totally suppressed, the palladium species can undergo a number of reactions with the formation

of new C—C bonds. With an appropriate choice of substrates, these transformations can occur as a sequence of events in a single synthetic operation.

The same range of termination can be found within the coupling of alkynes and 1,1-disubstituted alkenes.

C.i.b. Six-Centered Processes. Allylpalladium compounds, which are readily accessible, for example, by allylic substitution on allyl esters or by carbopalladation of 1,2-dienes or 1,3-dienes with or without subsequent rearrangement (**Scheme 7**, Eq. 1), may



add to π -bond systems with the formation of new C—C bonds in a so-called metalla-ene reaction via a six-centered transition structure (**Scheme 7**, Eqs. 2,3) (**Sect. IV.4**). The thus formed σ -alkyl- or σ -alkenylpalladium species can subsequently undergo any of the typical reactions.

D. CATALYST SYSTEM AND OTHER BASIC CONDITIONS FOR CARBOMETALLATION REACTIONS

The most frequently used catalyst systems for Heck-type coupling reactions consist of commercially available palladium compounds in the presence of various ligands. The first choice is often the air-stable and relatively inexpensive palladium acetate; however, several of the other published variants can be preferable for certain applications. It is commonly assumed that the palladium(II) species is reduced *in situ* by the solvent, the alkene,^[27] the amine,^[28] or the added ligand (frequently a phosphane, which is oxidized to a phosphane oxide).^{[29],[30]} In some cases, highly dispersed elemental palladium on charcoal can be applied. This can be an advantageous catalyst system, since it can be used for the hydrogenation of the formed double bond in the same operation.^{[31]–[33]} In the cases of alkenyl or aryl bromides, phosphanes are necessary to avoid precipitation of palladium black, whereas iodides have been reported to be less reactive in the presence of phosphanes. Triflates have been found to be more reactive in the presence of chloride ions, as the chloride ligand is more easily removed from palladium than the triflate ion. Yet successful coupling reactions of alkenyl triflates have also been performed in the absence of chloride ions.^{[23],[34]}

It has been shown that palladacycles,^{[35]–[39]} prepared from palladium(II) acetate and the tris(*o*-tolyl)- or trimesitylphosphane, are excellent catalysts for the Heck coupling of triflates and halides including activated aryl chlorides. In this case, oxidation states +II and +IV of palladium have been invoked in the catalytic cycle.^[35]

In some cases, reasonably stable palladium(0) complexes derived from dibenzylideneacetone [such as Pd(dba)₂, Pd₂(dba)₃, or Pd₂(dba)₃·CHCl₃] can be utilized advantageously, especially when the substrate is sensitive toward oxidation.

Initially, only dipolar aprotic solvents such as tertiary amines, acetonitrile (MeCN), dimethylformamide (DMF), *N*-methylpyrrolidinone (NMP), and dimethylsulfoxide (DMSO), were common. However, as originally observed by Heck,^[40] the presence of water can accelerate certain coupling reactions,^{[41]–[45]} and consequently the development has gone to water-soluble triarylphosphane ligands (e.g., triphenylphosphane *m*-trisulfonate sodium salt (TPPTS)^{[46]–[48]}) with which many alkene arylations superbly succeed in aqueous solvent mixtures.^{[49],[50]}

Recent developments have shown that supercritical carbon dioxide can favorably be applied as a solvent in the presence of palladium on charcoal^[51] or palladium trifluoroacetate.^[52]

D.i. Effects of Bases, Ligands, and Additives

A major achievement was the discovery that Heck reactions are greatly accelerated in the presence of quaternary ammonium salts and solid bases [“Jeffery” conditions: Pd(OAc)₂, K₂CO₃ (or Na₂CO₃ or NaHCO₃), *n*-Bu₄NX (X = Br, Cl), DMF (or NMP, DMSO)].^{[53],[54]} Under these conditions iodoarenes and iodoalkenes can be coupled to alkenes at room

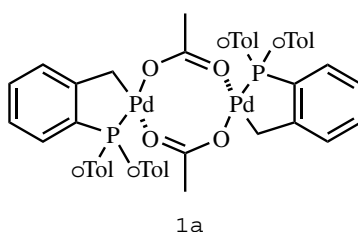
temperature. The assistance of tetraalkylammonium salts in the regeneration of the catalytically active palladium(0) species apparently plays the major role.^[55]

D.ii. Leaving Groups

The Heck reaction can be used to couple alkenyl, aryl, allyl (the intramolecular Heck reaction on allylic substrates is called a palladaene reaction),^{[10],[11],[56],[57]} benzyl, methyl, alkoxycarbonylmethyl, alkynyl,^[12] certain alkyl,^{[13],[58]} and silyl^[59] fragments to a variety of alkenes. The nature of the leaving group greatly affects the reaction rate: aryl iodides react faster than bromides,^[60] and aryl chlorides are notoriously unreactive unless special catalysts or ligands and elevated temperatures are used to enhance the reaction rate. This has been taken to indicate that the oxidative addition of the haloarene (haloalkene) to palladium(0) is the rate-determining step.^{[61]–[68]} It has been shown that the Heck reaction can be performed with aryldiazonium salts,^{[32],[69]–[74]} *N*-nitroso-*N*-arylacetamides,^[75] and hypervalent iodo compounds^{[76]–[78]} at room temperature.

The coupling of low-cost chloroarenes using specially designed palladium catalysts, allowing high turnover rates, has been reported by Herrmann and Beller et al.^[79] Alkenyl perfluorosulfonates have gained importance as substitutes for haloalkenes—at least in laboratory scale preparations—as they are easily obtained from the corresponding carbonyl compounds.^[23] Many successful reactions with alkenyl trifluoromethanesulfonates (alkenyl triflates) took advantage of this leaving group. The previously observed inhibition of the overall coupling reaction following facile oxidative addition of the alkenyl triflate to palladium(0) can be prevented by adding lithium chloride to the reaction mixture. Aryl iodides, however, are more reactive than the corresponding triflates^{[19]–[21],[80]}

The coupling reaction can be accelerated by applying high pressure.^{[81]–[87]} The influence of high pressure on the Heck reactions of selected alkenyl and aryl halides, that is, 1-iodocyclohex-1-ene, iodobenzene, and bromobenzene with methyl acrylate, has been investigated and the activation parameters of these reactions determined.^[88] Two different catalyst cocktails were used in this study, the classical system [Pd(OAc)₂, NEt₃, PPh₃] and the palladacycle **1a** as prepared from Pd(OAc)₂ and P(*o*-Tol)₃ by Herrmann, Beller, and co-workers.^{[35],[36]} The temperature-dependent and the pressure-dependent rate coefficients both follow the order Ph-I/Pd(OAc)₂ > 1-iodocyclohexene/Pd(OAc)₂ > Ph-I/**1a** > Ph-Br/**1a** and the activation enthalpies as well as the activation entropies exhibit the trend 1-iodocyclohexene/Pd(OAc)₂ < Ph-I/Pd(OAc)₂ < Ph-I/**1a** < Ph-Br/**1a**. The absolute values of the activation volumes, which were ascertained from the pressure-dependent rate coefficients, increase as follows: 1-iodocyclohexene/Pd(OAc)₂ < Ph-I/Pd(OAc)₂ ≈ Ph-I/**1a** < Ph-Br/**1a**. Under high pressure, the lifetime of the active palladium catalyst and thereby the turnover numbers are greatly increased.^{[81]–[83]}



The Heck reaction can also be performed under microwave irradiation and thus be drastically accelerated (typically 3–4 min reaction time at room temperature, compared to a few hours at elevated temperatures). In this case, DMF has proved to be an excellent solvent.^[89]

It has been shown that chloroarenes can be activated for oxidative addition onto palladium(0) catalysts through the formation of the corresponding tricarbonylchromium complexes,^{[90]–[92]} as the (CO)₃Cr group exerts a strong electron-withdrawing effect on the arene moiety, by using (bulky) bidentate phosphanes (e.g., dippb or even dppe).^{[93]–[96]}

The Heck reaction is compatible with a variety of substituents; only strong oxidizing agents such as quinones or TCNE are not tolerated.

D.iii. Stereochemical Requirements in Intramolecular Cyclizations

For the design of natural products syntheses, a predictability of the regioselectivity is required. However, all ring sizes from three- to nine-membered are attainable, either by *exo-trig* for three- to nine-membered or *endo-trig* cyclizations for six- to nine-membered rings. Applications toward the construction of larger rings (sizes 13–24) have been demonstrated using solid support in combinatorial syntheses (**Sect. X.3**) and by employing slow addition of the substrate and/or high dilution techniques.^[97]

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