

II.3.2 Stoichiometric Synthesis and Some Notable Properties of Organopalladium Compounds of Pd(0) and Pd(II)

DANIELE CHOUÉIRY

A. INTRODUCTION

As discussed in **Sect. I.2**, palladium complexes of general formula PdL_n can react according to well-defined reaction patterns that lead to organopalladium complexes through C—Pd bond formation. These general patterns were largely discussed in **Sect. II.3.1**. While these principles are most often used to generate *in situ* organopalladium species, under catalytic conditions, they have also been applied to the preparation of discrete organopalladium entities in a stoichiometric way. Isolation of organopalladium complexes is important not only in the preparation of organopalladium catalysts, but also for mechanistic investigations. Indeed, it is through the understanding of both their reactivity and the rules governing their formation that the discovery of new catalytic reactions via organopalladium complexes can be significantly facilitated.

Palladium forms complexes with a variety of carbon ligands. The carbon ligand may be neutral or charged, and sp³, sp², or sp hybridized. Pd complexes of neutral carbon ligands, such as CO and alkenes, are typically generated by complexation reactions, while oxidative addition, hydro-, carbo-, and heteropalladation reactions, and transmetalation provide major routes to the organopalladium complexes containing a σ C—Pd bond. The reactivity of organopalladium complexes is also indicated by the general patterns (**Sect. II.3.1**). While some of these patterns, such as carbometallation and migratory insertion, result in new organopalladium species, some others, such as reductive elimination or nucleophilic attack on ligands, result in the destruction of organopalladium species.

B. PALLADIUM COMPLEXES CONTAINING NEUTRAL CARBON LIGANDS ONLY

Palladium forms complexes with a variety of neutral carbon ligands. While some of them, such as CO and isonitriles, bind to palladium in a σ- or μ-fashion, others, such as alkenes, dienes, and alkynes, form π-complexes.

B.i. σ - and μ -Carbon Ligands: Carbonyl and Isonitrile Complexes

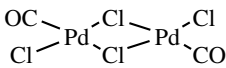
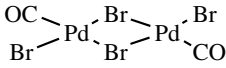
The chemistry of palladium–carbonyl complexes has experienced extensive recent developments due to an increased interest in the role of palladium in surface catalysis especially in automobile exhaust catalysts. Palladium–carbonyl complexes are nevertheless still relatively rare, which is probably due to their relative instability in comparison with that of Ni complexes. The homoleptic $\text{Pd}(\text{CO})_4$ only exists at low temperatures (<80 K) in noble gas or CO matrices, in sharp contrast with isoelectronic $\text{Ni}(\text{CO})_4$, which is stable at ambient temperature. **Table 1** compiles some of the known and representative carbonyl complexes of palladium.

In cases of dinuclear Pd–carbonyl complexes, the carbonyl ligand can be linear [i.e., $\text{Pd}(\sigma\text{-CO})$] or bridging [i.e., $\text{Pd}_2(\sigma\text{-CO})$]. Actually, the great majority of dinuclear Pd carbonyls have carbonyl-bridged structures. However, most of these complexes are Pd(I) complexes and will not be covered in this section. An exception is the Pd(II) complex, $\text{Pd}_2(\text{CO})_2\text{Cl}_4$, in which the CO ligands are terminal.

Palladium–carbonyl complexes are typically formed from PdX_2 ($\text{X} = \text{Cl}, \text{Br}, \text{or I}$) and CO. For example, $\text{Pd}_2(\text{CO})_2\text{Cl}_4$ is obtained by high-pressure carbonylation of PdCl_2 . Similarly, the anionic $\text{M}[\text{Pd}(\text{CO})\text{X}_3]$ are obtained from carbonylation of PdX_2 or $\text{M}_2(\text{Pd}_2\text{X}_6)$. While the iodide is relatively unstable, the chloride and bromide could be characterized by X-ray crystallography.^[4]

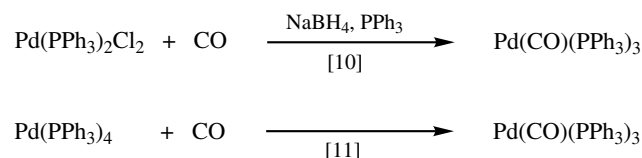
Alternatively, CO can displace a variety of ligands from palladium and Pd–CO complexes have been prepared from Pd–nitrile and even Pd–phosphine complexes. For instance, $\text{Pd}(\text{CO})_2\text{Cl}_2$ has been obtained via ligand displacement of $\text{Cl}_2\text{Pd}(\text{PhCN})_2$ with CO. In cases of Pd(0) complexes, the starting materials can be either Pd(0) species, such as $\text{Pd}(\text{PPh}_3)_4$, or Pd(II) species, such as $\text{Cl}_2\text{Pd}(\text{PPh}_3)_2$. In the latter cases, the use of added reducing agents may be desirable or necessary, as in the preparation of $\text{Pd}(\text{CO})(\text{PPh}_3)_3$ (**Scheme 1**).^[10] Alternatively, this same complex can be obtained from $\text{Pd}(\text{PPh}_3)_4$ and CO

TABLE 1. Palladium–Carbonyl Complexes

Carbon Number ^a	Pd–Carbonyl Complex	Comments	References for Preparation
MONOMERS			
1	$\text{M}[\text{Pd}(\text{CO})\text{Cl}_3]$	$\text{M} = \text{Et}_2\text{H}_2\text{N}, \text{Bu}_4\text{N}$	[1],[2]
	$\text{M}[\text{Pd}(\text{CO})\text{Br}_3]$	$\text{M} = \text{K}, \text{Bu}_4\text{N}$	[1],[3]
	$\text{M}[\text{Pd}(\text{CO})\text{I}_3]$	$\text{M} = \text{Bu}_4\text{N}$; readily loses CO	[4]
	$\text{M}[\text{Pd}(\text{CO})\text{Cl}(\text{SnCl}_3)_2]$	$\text{M} = \text{Et}_4\text{N}$	[5]
2	$\text{Pd}(\text{CO})_2\text{Cl}_2$		[6]
4	$\text{Pd}(\text{CO})_4$	Only by matrix isolation	[7]
13	$[\text{Pd}(\text{CO})(\text{PEt}_3)_2\text{Cl}]\text{X}$	$\text{X} = \text{BF}_4$; readily loses CO	[8]
21	$\text{Pd}[\text{CO}]_3(\text{PPh}_3)$	Only under CO pressure	[9]
55	$\text{Pd}(\text{CO})(\text{PPh}_3)_3$		[10],[11]
DIMERS			
1			[2]
			[4]

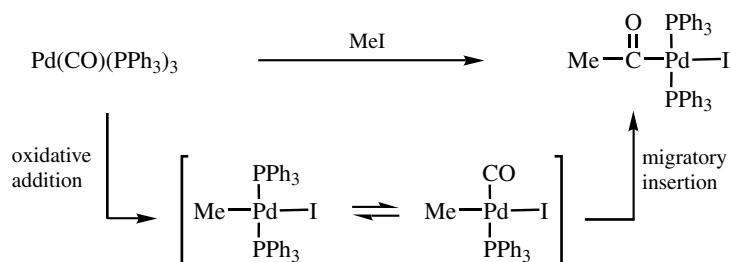
^aNumber of C atoms in a monomer unit.

(**Scheme 1**).^[11] Palladium–carbonyl complexes can themselves be the source of other carbonyl complexes. For example, $(\text{Et}_2\text{H}_2\text{N})[\text{Pd}(\text{CO})\text{Cl}_3]$ can be obtained from $\text{Pd}_2\text{Cl}_4(\text{CO})_2$ and $\text{Et}_2\text{H}_2\text{NCl}$.^[12]



Scheme 1

The most interesting feature of the reactivity of Pd–CO complexes is their migratory insertion reaction that takes place in cases where the Pd–CO complex simultaneously contains an additional C–Pd bond. This migratory insertion of CO leads to the formation of acyl–Pd complexes. Indeed, Pd(0) complexes of CO, such as $\text{Pd}(\text{CO})(\text{PPh}_3)_3$, can react with methyl iodide, allyl chloride, and vinyl chloride, to give the corresponding acyl–Pd complexes (**Scheme 2**).^[10] This transformation can be explained in terms of an oxidative addition–migratory insertion sequence (**Scheme 2**). Acyl–Pd complexes will be discussed in greater detail in **Sect. C.ii**.



Scheme 2

This reaction profile, also called carbonylation, governs the reactivity of Pd–carbonyl complexes. Anionic $\text{M}[\text{Pd}(\text{CO})\text{I}_3]$, for instance, catalyzes the reductive carbonylation of esters.^[12] On the other hand, $\text{Pd}(\text{CO})(\text{PPh}_3)_3$ was reported to catalyze the carboxymethylation of organic halides^[13] and the cyclocarbonylation of cinnamyl halides.^[14] However, the Pd–CO complexes are most often generated *in situ* from preformed alkyl–palladium complexes and CO under stoichiometric^[15] or catalytic conditions, for example, in the copolymerization of alkenes and CO.^[16] Decarbonylation reactions also involve the intermediacy of Pd–CO complexes. In this case, migratory deinsertion (**Sect. II.3.1**), that is, the microscopic reversal of the migratory insertion, takes place.

Closely related to the palladium–carbonyl complexes are the palladium–isonitrile complexes. Isonitriles are better σ -donors than the isoelectronic CO and are consequently better ligands for Pd than CO. Their Pd complexes are indeed more stable than the corresponding CO complexes. Isonitrile–palladium complexes are usually prepared from PdX_2 ($\text{X} = \text{Cl}, \text{Br}, \text{I}$), or their derivatives, for example, Na_2PdCl_4 , and $\text{Cl}_2\text{Pd}(\text{CH}_3\text{CN})_2$, via ligand exchange. Occasionally, organopalladium complexes such as $(\eta^5\text{-C}_5\text{H}_5)$

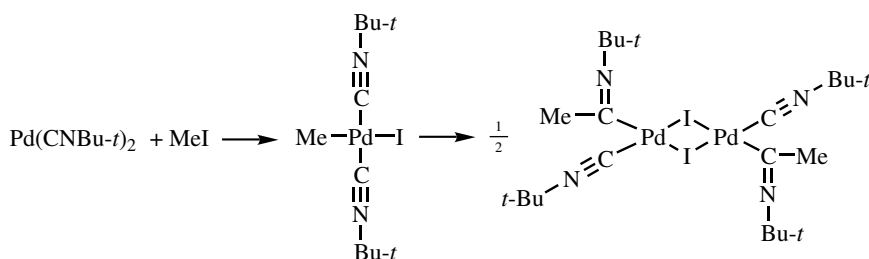
TABLE 2. Palladium–Isonitrile Complexes

Carbon Number	Pd–Isonitrile Complex	Comments	References for Preparation
8	$\text{Pd}[(\text{CNMe})_4]\text{X}_2$	$\text{X} = \text{BF}_4, \text{PF}_6$	[17],[18]
10	$\text{Pd}(\text{CNBu-}t)_2$		[19]
	$\text{Pd}(\text{CNBu-}t)_2\text{Cl}_2$	<i>cis</i>	[20]
	$\text{Pd}(\text{CNBu-}t)_2\text{I}_2$	<i>trans</i>	[19]
	$\text{Pd}(\text{CNBu-}t)_2\text{O}_2$		[19]
14	$\text{Pd}\left(\text{CN}-\text{C}_6\text{H}_{11}\right)_2\text{X}_2$	$\text{X} = \text{Cl, I; cis}$	[21]

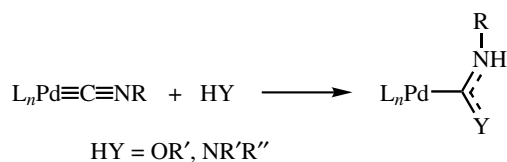
$(\eta^3\text{-C}_3\text{H}_5)\text{Pd}$ (Sect. C.i) serve as precursors to Pd–isonitrile complexes, for example, $\text{Pd}(\text{CNR})_2$. Finally, Pd–isonitrile complexes can also serve as precursors to other Pd–isonitrile complexes. An example is provided by the preparation of $\text{Pd}(\text{CNBu-}t)_2\text{O}_2$ from $\text{Pd}(\text{CNBu-}t)_2$. Table 2 lists some representative Pd–isonitrile complexes.

Like Pd–CO complexes, Pd–isonitrile complexes can undergo oxidative addition into carbon–halide bonds, and then subsequent migratory insertion, as exemplified in Scheme 3.^[22]

Another interesting reaction of Pd(II)–isonitrile complexes is that with protic compounds to produce palladium–carbene complexes (Scheme 4).^[23]



Scheme 3

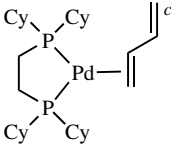
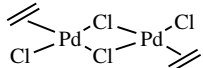
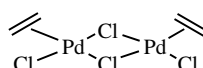
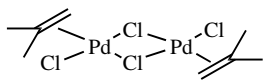
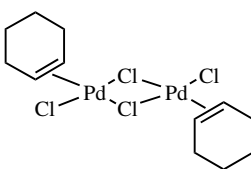
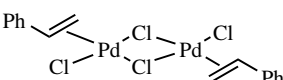


Scheme 4

B.ii. η^2 -, η^4 -Carbon Ligands (π -Complexes): Alkenes, Dienes, and Alkynes Complexes

Many examples of Pd–alkene, Pd–diene, and Pd–alkyne complexes are known for both Pd(0) and Pd(II) oxidation states. Representative examples are given in Tables 3, 4, and 5.

TABLE 3. Palladium–Monoene π -Complexes

Carbon Number ^a	Pd–Monoene Complex	Comments	References for Preparation
MONOMERS			
2	$M[Pd(H_2C=CH_2)Cl_3]$	$M = Bu_4N$; unstable at r.t. ^b	[24]
4	$Pd(H_2C=CH_2)_2Cl_2$	Stable under C_2H_4	[25]
6	$Pd(H_2C=CH_2)_3$	Stable under C_2H_4	[26]
21	$Pd(\text{norbornene})_3$		[26]
30		Stable at 0 °C	[27]
38	$Pd(H_2C=CH_2)(PPh_3)_2$	Air-sensitive	[28]
	$Pd(H_2C=CH_2)(PCy_3)_2$	Air-sensitive	[28]
40	$Pd(\text{maleonitriledithiolene})(PPh_3)_2$	Air-stable	[29]
51	$Pd(dba)_3$ ^d	Unstable	[30]
96	$Pd(\eta^2-C_{60})(PPh_3)_2$		[31]
DIMERS			
2		<i>trans</i>	[32],[33]
		<i>cis</i>	[34]
4			[32]
6			[32]
8			[32]

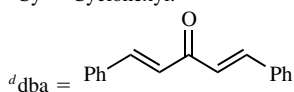
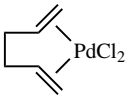
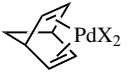
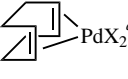
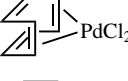
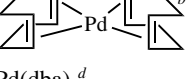
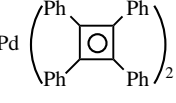
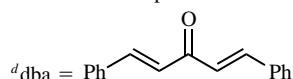
^aNumber of C atoms in a monomer unit.^br.t. = room temperature.^cCy = Cyclohexyl.

TABLE 4. Palladium–Diene and Palladium–Polyene π -Complexes

Carbon Number	Pd Complex	Comments	References for Preparation
DIENE COMPLEXES			
6			[35]
7		X = Cl, Br	[36]
8		X = Cl, Br, I; commercially available for X = Cl	[37],[38]
		Air-sensitive	[39]
16		Stable below r.t. ^c	[26]
34	$\text{Pd}(\text{dba})_2^d$		[40]
51	$\text{Pd}_2(\text{dba})_3^d$		[41]
56			[42]
POLYENE COMPLEXES			
60	$\text{Pd}(\text{C}_{60})$		[43]

^a $\text{Pd}(1,5\text{-cyclooctadiene})\text{Cl}_2$ or $\text{Pd}(1,5\text{-cod})\text{Cl}_2$.^b $\text{Pd}(1,5\text{-cod})_2$.^cr.t. = room temperature.

Alkene complexes of Pd(0) can be obtained from either Pd(0) or Pd(II) precursors. For example, $\text{Pd}(\text{H}_2\text{C}=\text{CH}_2)_3$ (**Table 3**) is obtained by the condensation of Pd atoms with ethylene, or via ligand displacement from $\text{Pd}(1,5\text{-cod})_2$ (**Table 4**),^[26] which, in turn, is obtained by the reduction of $\text{Pd}(1,5\text{-cod})\text{Cl}_2$ in the presence of 1,5-cyclooctadiene.^[26]

Likewise, mixed alkene/phosphine Pd(0) complexes, for example, $\text{Pd}(\text{alkene})(\text{PR}_3)_2$, can be obtained either by the reduction of a Pd(II) species, such as $\text{Pd}(\text{acac})_2$ or $\text{Pd}(\text{OAc})_2$, in the presence of the desired alkene and phosphine,^[28] or by the reaction of $\text{Pd}(\text{PR}_3)_4$ with the desired alkene.^[29] Dienes and polyenes can also serve as ligands in such complexes. In these cases, however, they act as monoenes, for example, $\text{Pd}(\eta^2\text{-1,3-butadiene})(\text{Cy}_2\text{PC}_2\text{H}_4\text{PCy}_2)$ and $\text{Pd}(\eta^2\text{-C}_{60})(\text{PPh}_3)_2$, and are consequently classified in **Table 3**. Alkene complexes of Pd(0) are usually less stable than their Ni or Pt analogs, but electron-withdrawing groups in alkenes stabilize the resulting complexes, for example, $\text{Pd}(\text{maleic anhydride})(\text{PPh}_3)_2$.^[29] Alkynes containing electron-withdrawing groups behave

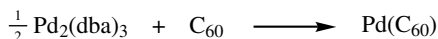
TABLE 5. Palladium–Alkyne π -Complexes

Carbon Number ^a	Pd Complex	References for Preparation
MONOMERS		
20	$\text{Pd}(\text{CF}_3\text{C}\equiv\text{CCF}_3)(\text{PPhMe}_2)_2$	[44]
32	$\text{Pd}(\text{MeOOC}\equiv\text{CCOOMe})(\text{Cy}_2\text{PCH}_2\text{CH}_2\text{PCy}_2)$	[27]
40	$\text{Pd}(\text{CF}_3\text{C}\equiv\text{CCF}_3)(\text{PPh}_3)_2$	[44]
	$\text{Pd}(\text{PhC}\equiv\text{CPh})_2(\text{C}_6\text{F}_5)_2$	[45]
42	$\text{Pd}(\text{MeOOC}\equiv\text{CCOOMe})(\text{PPh}_3)_2$	[44]
DIMERS		
10	$[\text{Pd}(t\text{-BuC}\equiv\text{CBu-}t)\text{Cl}_2]_2$	[46]

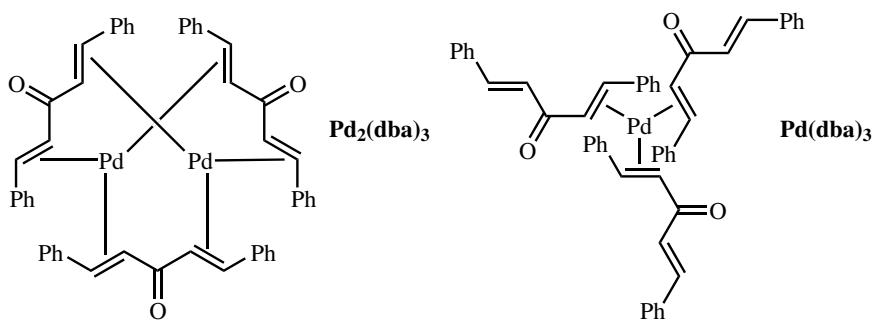
^aNumber of C atoms in a monomer unit.

similarly to form relatively stable mixed alkyne/phosphine–Pd complexes and are prepared in manners similar to those of their alkenes analogs (**Table 5**).

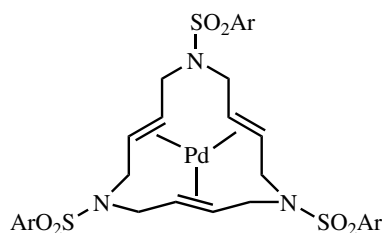
Some of the synthetically important Pd–alkene π -complexes include $\text{Pd}(\text{dba})_2$ and $\text{Pd}_2(\text{dba})_3$, which are stable to air and commercially available. The ease of displacement of the dba ligands by a variety of ligands including phosphines is at the origin of their extensive use as Pd(0) precursors, for both stoichiometric preparation (**Scheme 5**)^[43] and *in situ* generation of Pd(0) species.^{[47],[48]} The role of dba in the reactions of Pd(0) complexes *in situ* generated from $\text{Pd}(\text{dba})_2$ and phosphines has been thoroughly investigated in the past few years.^[49]

**Scheme 5**

It is worth noting that $\text{Pd}(\text{dba})_2$ and $\text{Pd}_2(\text{dba})_3$ are structurally closely related complexes in which the dba act as η^4 ligands (**Scheme 6**). Recrystallization of $\text{Pd}(\text{dba})_2$, which actually is better represented by $[\text{Pd}_2(\text{dba})_3](\text{dba})$, from chloroform, benzene, or toluene leads to $[\text{Pd}_2(\text{dba})_3](\text{solvent})$.^[41] On the other hand, $\text{Pd}(\text{dba})_3$ is obtained by the addition of an excess of dba to $\text{Pd}(\text{dba})_2$. In this case, dba acts as an η^2 ligand (**Scheme 6**).^[30]

**Scheme 6**

It should be noted that $\text{Pd}(\text{dba})_2$ and $\text{Pd}_2(\text{dba})_3$ have also proved to be useful as “ligandless” catalysts, that is, without added P-, As-, or N-containing ligands, in Pd-catalyzed processes, such as the Suzuki coupling.^{[50],[51]} This is an important development considering the toxicity of the frequently used phosphine or arsine ligands. Recently, an interesting Pd(0)–triolefin complex of a phosphine-free 15-membered macrocyclic ligand (**Scheme 7**) has been prepared and proved useful as a recoverable catalyst in cross-coupling reactions.^[52]

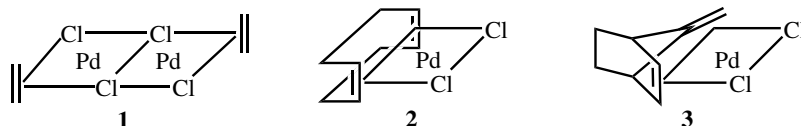


Scheme 7

Pd(II) complexes are electrophilic species, and they readily coordinate alkenes, dienes, and alkynes. These complexes are typically prepared from PdCl_2 and its derivatives, for example, Li_2PdCl_4 and Na_2PdCl_4 , or $\text{Cl}_2\text{Pd}(\text{PhCN})_2$, and the corresponding π -carbon ligand. This reaction leads to monomeric Pd complexes in the case of dienes (**Table 4**), while the use of alkenes and alkynes leads to the formation of dimeric species (**Tables 3 and 5**). The reaction of $\text{Cl}_2\text{Pd}(\text{PhCN})_2$ with ethylene, for instance, leads to the formation of $[\text{Pd}(\text{CH}_2=\text{CH}_2)\text{Cl}_2]_2$, which can be converted into $\text{Pd}(\text{CH}_2=\text{CH}_2)_2\text{Cl}_2$ only under a high pressure of ethylene.^[25] Alternatively, $[\text{Pd}(\text{alkene})\text{Cl}_2]_2$ can react with another alkene or an alkyne to generate a new Pd–alkene or Pd–alkyne complex via ligand exchange. As $\text{Pd}(\text{PhC}\equiv\text{CPh})_2(\text{C}_6\text{F}_5)_2$ is a rare example of stable bisacetylene Pd(II) complexes, it is listed in **Table 5** despite the presence of two uninegative C_6F_5 groups.

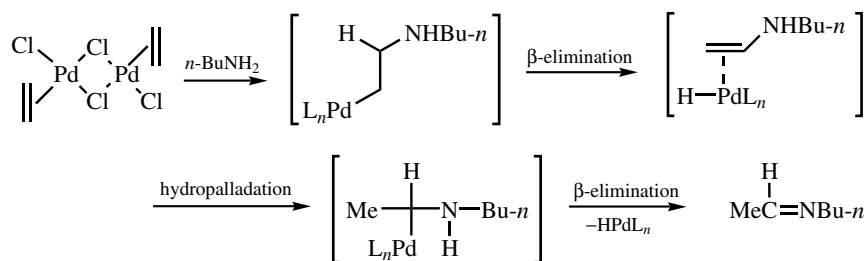
As in the cases of carbonyl complexes, anionic complexes of alkenes, for example, $(\text{Bu}_4\text{N})[\text{Pd}(\text{CH}_2=\text{CH}_2)\text{Cl}_3]$, have been generated by the reaction of the corresponding alkene with $(\text{Bu}_4\text{N})_2\text{Pd}_2\text{Cl}_6$.^[24]

From the structural viewpoint, it is interesting to note that alkene and diene complexes of Pd(II), such as $[\text{Pd}(\text{CH}_2=\text{CH}_2)\text{Cl}_2]_2$ (**1**) and $\text{Pd}(1,5\text{-cod})\text{Cl}_2$ (**2**), have, for steric reasons, the double bond C—C axis perpendicular to the Pd square plane (**Scheme 8**).^[53] In some cases, however, one alkene can be constrained to lie in the coordination plane of Pd, as exemplified by **3**.^[54]

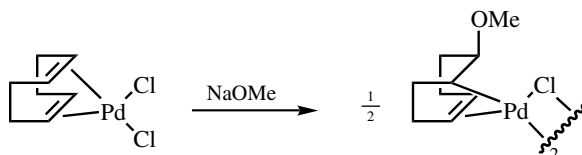


Scheme 8

One of the most remarkable features associated with the $\text{Pd}-(\pi\text{C}=\text{C})$ complexes is the high reactivity of the π -ligands toward nucleophiles rather than electrophiles. Whereas alkenes, dienes, and alkynes generally react readily with electrophiles, those coordinated with $\text{Pd}(\text{II})$ species react with nucleophiles, such as water, alkoxides, alcohols, amines, and carbon nucleophiles, such as malonic ester anions and Grignard reagents. These nucleophilic attacks induce the transformation of $\text{Pd}-(\pi\text{C}=\text{C})$ complexes into new palladium complexes containing a σ $\text{C}-\text{Pd}$ bond, resulting in an overall hetero- or carbopalladation process. Butylamine, for instance, reacts with $[\text{Pd}(\text{CH}_2=\text{CH}_2)\text{Cl}_2]_2$ to give $\text{MeCH}=\text{NBu}-n$ by the nucleophilic attack of the amine on the Pd -coordinated ethylene followed by *syn* β -elimination and 1,3-hydrogen shift (**Scheme 9**).^[55] On the other hand, the reaction of sodium methoxide with $\text{Pd}(1,5\text{-cod})\text{Cl}_2$ leads to a new $\text{Pd}(\text{alkene})(\text{alkyl})$ complex (**Scheme 10**).^[37]

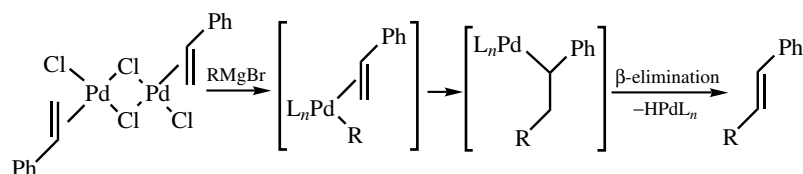


Scheme 9



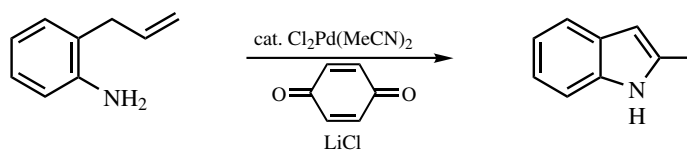
Scheme 10

These nucleophilic attacks proceed in an intermolecular fashion and give the *anti* or *exo* addition products. This has been clearly demonstrated in the reaction of $\text{Pd}(1,5\text{-cod})\text{Cl}_2$ with sodium methoxide,^[37] which has yielded a complex analyzed by NMR spectroscopy.^[56] On the contrary, *syn* or *endo* addition takes place when Grignard reagents are used. In these cases, transmetalation leading to the formation of a σ $\text{C}-\text{Pd}$ bond takes place first (**Scheme 11**).^[57] As a result, the nucleophile is delivered intramolecularly in a *syn* or *endo* fashion, via a carbopalladation reaction (**Scheme 11**).^[57]



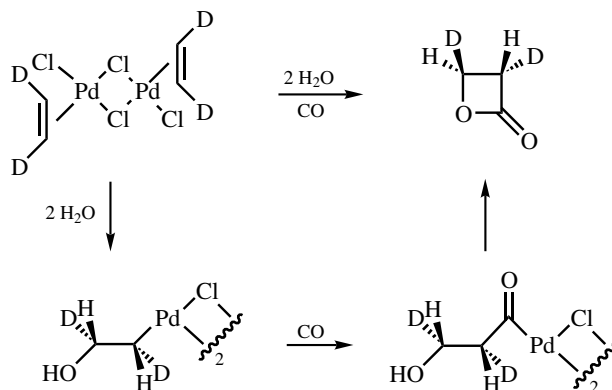
Scheme 11

Alkene–Pd, diene–Pd, or alkyne–Pd complexes can be useful catalysts or catalyst precursors for many organic transformations. In addition to the widely used Pd–dba complexes (*vide supra*), other Pd–alkene complexes have shown some interesting catalytic activity. For instance, Pd(1,5-cod)Cl₂, which is commercially available, catalyzes the selective protection of primary alcohols as acetals under neutral conditions.^[58] Another example is Pd(maleic anhydride)(PPh₃)₂, which has been used as a catalyst in the reaction of allene with diolefins,^[59] amines,^[60] or active hydrogen compounds.^[60] Besides its high stability, its high solubility in organic solvents makes this π -complex a convenient catalyst. A catalytic quantity of Pd(CH₂=CH₂)(PPh₃)₂ was found to induce the alkylation of (Z)-3-acetoxy-5-carbomethoxy-1-cyclohexene with dimethylmalonate,^[61] leading to a more extensive stereochemical scrambling than Pd(PPh₃)₄ in a process in which a high phosphine/Pd ratio seems important. Finally, [Pd(CH₂=CH₂)Cl₂]₂ and [Pd(cyclohexene)Cl₂]₂ were found to be as good as Cl₂Pd(PhCN)₂ and PdCl₂ in the catalytic isomerization of olefins, indicating that all of these catalyst precursors are converted to a common Pd–olefin intermediate that must serve as the actual catalyst.^[62] Indeed, Pd–alkene, Pd–diene, or Pd–alkyne π -complexes have often been assumed to be the actual catalysts in several Pd-catalyzed transformations, and the stoichiometric preparation and isolation of some of them provide a strong support for their intermediacy. An example of a process involving the likely intermediacy of an alkene–Pd complex is provided by the Cl₂Pd(MeCN)₂-catalyzed transformation of *o*-allylanilines to indoles (Scheme 12).^[63]



Scheme 12

Another well-known example is the Wacker process known to proceed via a hydroxypalladation mechanism (Sect. V.3).^[64] The stereochemistry of the hydroxypalladation of alkenes was actually assessed by studying the reaction of the preformed [Pd(CD₂=CD₂)Cl₂]₂ with water under carbonylative conditions and was found to proceed in an *anti* fashion (Scheme 13).^[65]



Scheme 13

A recent application of the Pd(II)-induced activation of double or triple bonds toward nucleophilic attack is the development of an interesting one-pot synthesis of substituted tetrahydrofurans and pyrrolidines.^{[66]–[68]}

The ease with which nucleophiles add to alkenes and alkynes coordinated to Pd(II) combined with the tendency of Pd to form π -allyl complexes accounts for the limited number of Pd(II)–alkene, Pd(II)–diene, or Pd(II)–alkyne complexes. Indeed, as detailed in the next section, depending on the conditions or their structural features, alkenes, dienes, and alkynes often lead to the formation of π -allylpalladium complexes instead of η^2 or η^4 π -complexes. This is particularly true in the case of alkenes bearing hydrogens α to the double bond, 1,3-dienes, such as 1,3-butadiene, and alkynes of low steric hindrance. In marked contrast, Pd(1,5-hexadiene)Cl₂ is obtained from the reaction of Cl₂Pd(PhCN)₂ with allyl chloride.^[35]

C. Pd COMPLEXES CONTAINING ANIONIC CARBON LIGANDS

The majority of known organopalladium complexes contain anionic carbon groups, such as alkyl, benzyl, aryl, alkenyl, and alkynyl groups. Acylpalladium complexes also belong to this category. These organyl ligands form σ bonds with Pd. With allyl and cyclopentadienyl groups, Pd in most cases is simultaneously linked to an anionic carbon group through a σ bond and to one or two allylic C=C bonds through π -complexation. In such cases, η^3 -allylpalladium and η^5 -cyclopentadienylpalladium complexes are formed rather than the corresponding η^1 -allyl- or cyclopentadienylpalladium complexes.

C.i. σ - and π -Bonded Complexes of Palladium: π -Allyl and Cyclopentadienyl Complexes

A large variety of π -allylpalladium complexes have been isolated. Some representative examples of such complexes are shown in **Table 6**.

A large number of allylic compounds, such as allyl halides, allyl alcohols, allyl acetates, allyl trifluoroacetates, and also allyl Grignard reagents, react with palladium salts, such as PdCl₂ or Na₂PdCl₄, to give π -allylpalladium complexes. The reaction of Na₂PdCl₄ with allyl chloride in MeOH in the presence of CO leads to the formation of the dimeric complex Pd₂(η^3 -C₃H₅)₂(μ -Cl)₂.^[84] The role of CO in this reaction is to ensure the reduction of the Pd(II) species into a Pd(0) species (see **Sect. II.2.3**) necessary for the oxidative addition into the C—Cl bond (**Scheme 14**). In contrast, allylmagnesium chloride reacts with Pd(II)Cl₂ to produce homoleptic Pd(η^3 -C₃H₅)₂ via transmetalation (**Scheme 14**). It is interesting to note that this latter type of complexes exist in solution as a mixture of the *cis* and *trans* isomers, while the *trans* isomer is favored in the solid state (**Scheme 15**).^[96] These reactions can be applied to the formation of substituted η^3 -allylpalladium complexes.

Once Pd₂(η^3 -C₃H₅)₂(μ -Cl)₂ and Pd(η^3 -C₃H₅)₂ are prepared, they can be transformed into a variety of other allylpalladium species, as exemplified in **Scheme 16**. Alternative direct synthetic routes starting from Pd(0) or Pd(II) species have also been utilized (**Scheme 17**).

Cationic allylpalladium complexes represented by [(η^3 -C₃H₅)PdL₂]⁺X[−] can be generated by the reaction of the dimeric Pd₂(η^3 -C₃H₅)₂(μ -X)₂, where X is Cl or Br, with salts of non-coordinating anions, for example, NaBPh₄ or AgBF₄, in the presence of ligands such as

TABLE 6. Allylpalladium Complexes

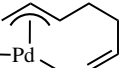
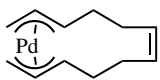
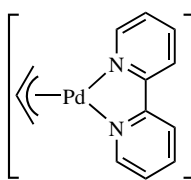
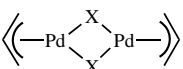
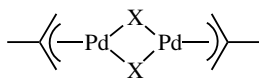
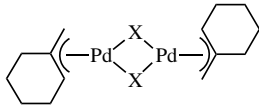
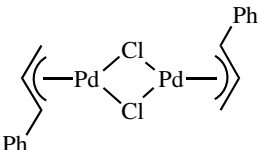
Carbon Number ^a	Pd Complex	Comments	References for Preparation
MONOMERS			
3	$\left[\left(\left(\text{---PdX}_2 \right) \right) \text{Ph}_4\text{P} \right]$	X = Cl, Br	[69]
6	$\left(\left(\text{---Pd---} \right) \right)$		[70]
8	$\text{---} \left(\left(\text{---Pd---} \right) \right) \text{---}$	Readily decomposes in solution	[71]
9	$\left(\left(\text{---Pd---} \right) \text{PMe}_3 \right)$	Unstable above 0 °C	[72]
	$\left(\left(\text{---Pd---} \right) \text{Br} \right) \text{PEt}_3$		[73]
11	$\text{Me}_3\text{P---Pd---}$ 	Air-sensitive; decomposes in solution above -25 °C	[74],[75]
12		Air-sensitive; decomposes above -20 °C	[76]
13	$\left[\left(\left(\text{---Pd---} \right) \text{N} \right) \right] \text{X}^b$ 	X = Br, BF ₄	[77]
15	$\left[\left(\left(\text{---Pd---} \right) \text{PEt}_3 \right) \right] \text{X}$	X = Br, BPh ₄	[78],[79]
21	$\left(\left(\text{---Pd---} \right) \text{PCy}_3 \right) \text{X}$	X = Br, AcO	[80],[81]
	$\left(\left(\text{---Pd---} \right) \text{Cl} \right) \text{PPh}_3$		[82]
DIMERS			
3	$\left(\left(\text{---Pd---} \right) \text{X} \right) \text{Pd---}$ 	X = Cl, Br, I, OAc; commercially available for X = Cl	[83]–[88]

TABLE 6. (Continued)

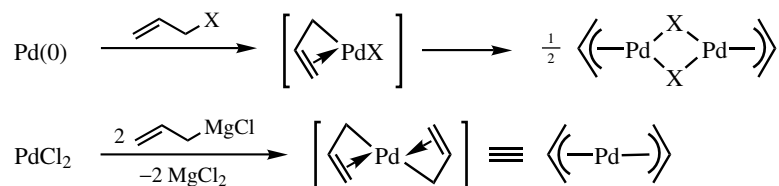
Carbon Number ^a	Pd Complex	Comments	References for Preparation
4		X = Cl, Br, I	[84],[87] [89]–[91]
7		X = Cl, Br	[92]–[94]
9			[90],[95]

^aNumber of carbons in a monomer unit.^b $[(\eta^3\text{-C}_3\text{H}_5)\text{Pd}(\text{bipy})]\text{X}$.

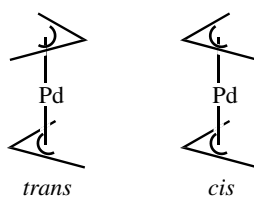
phosphines^[79] or bidentate amines, for example, bipy. Alternatively, this class of complexes can be obtained by the oxidative addition of allylic derivatives in the presence of an excess of ligand or chelating ligands. An interesting example is the preparation of $[(\eta^3\text{-C}_3\text{H}_5)\text{Pd}(\text{bipy})]\text{Br}$ from allyl bromide and $\text{Me}_2\text{Pd}(\text{bipy})$, demonstrating that dialkylpalladium species, which can be converted to Pd(0) species via reductive elimination (*vide infra*), can also be used to generate π -allyl complexes.^[77] With smaller amounts of ligands neutral $(\eta^3\text{-C}_3\text{H}_5)\text{Pd}(\text{L})\text{X}$ are obtained. It should be noted, however, that while the treatment of allyl acetate with $\text{Pd}(\text{PCy}_3)_2$ does provide the expected $(\eta^3\text{-C}_3\text{H}_5)\text{Pd}(\text{PCy}_3)\text{OAc}$ complex, the use of Pd–PPh₃ complexes, for example, $\text{Pd}(\text{PPh}_3)_4$, does not lead to the desired η^3 -allyl(acetato)palladium complexes.^{[80],[81]} This latter result is in agreement with a recent study, which provided evidence for the reversibility of the formation of π -allylpalladium complexes from the oxidative addition of Pd(0)–PPh₃ complexes into allyl acetate.^[97]

Some of these allylpalladium complexes, $\text{Pd}_2(\eta^3\text{-C}_3\text{H}_5)_2(\mu\text{-Cl})_2$ in particular, are important not only as precursors to a large variety of allylpalladium complexes, but also as Pd(0) sources in a variety of Pd-catalyzed processes.^[98] It is actually commercially available.

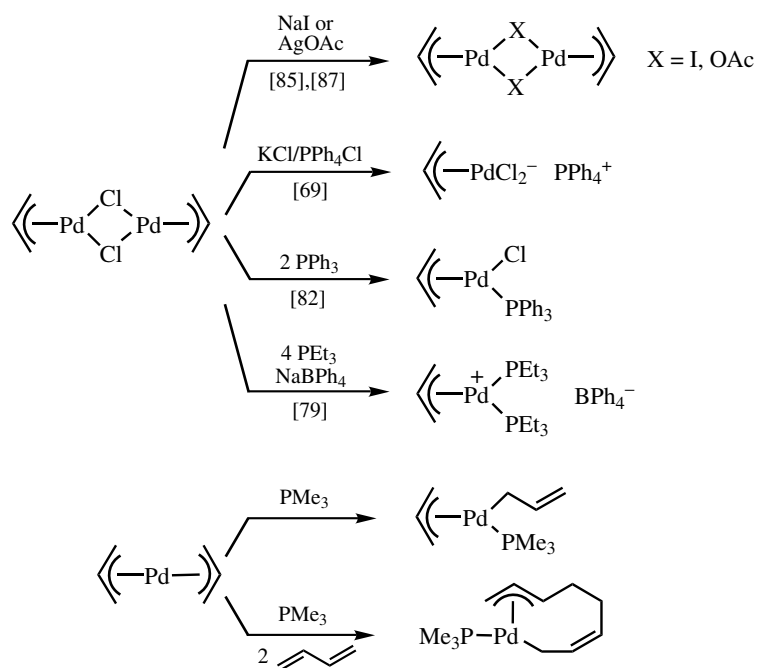
It is worth noting that in essentially all of the examples listed in Table 6 the isolated species correspond to the η^3 - π -allylpalladium complexes. The structure of $\text{Pd}_2(\eta^3\text{-C}_3\text{H}_5)_2(\mu\text{-Cl})_2$ has been determined by X-ray crystallography,^{[99],[100]} which has confirmed that the allyl group is bonded in an η^3 -mode occupying two coordination sites at an angle of about 110° relative to the plane of the Pd_2Cl_2 unit. It is indeed quite rare to isolate the σ -allylpalladium complexes, as they are usually less stable than the corresponding π -allyl derivatives. Mixed σ/π -allyl complexes could nonetheless be isolated by adding phosphines to bis(π -allyl)palladium complexes.^{[72],[74],[75]} It is important to keep in mind, however, that the two species can in principle interconvert in a dynamic equilibrium. This dynamic equilibrium has been clearly established for species such as $(\eta^3\text{-allyl})\text{PdX}(\text{PR}_3)$ in which interconversion between *syn* and *anti* substituents is rationalized by invoking the intermediacy of η^1 -allyl species.^[96]



Scheme 14



Scheme 15



Scheme 16

Alkenes can also react with Pd(II) salts to give π -allylpalladium complexes. One key requirement is that the alkene has one or more hydrogens α to the double bond that can be abstracted to give a π -allyl complex. Heat^{[89],[90]} or the presence of a base (**Scheme 18**),^[101] such as sodium carbonate or sodium acetate, favors the transformation of the initially formed η^2 -alkene complex into the π -allyl species.

istry is well defined.^[102]

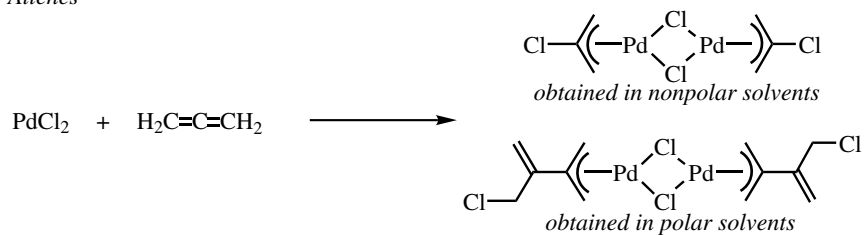
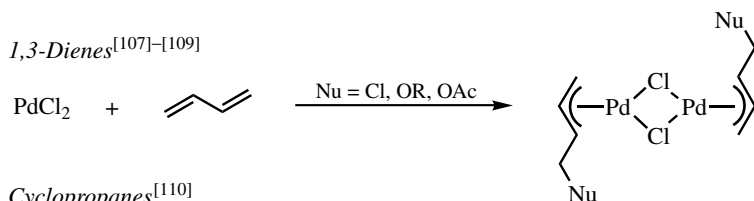
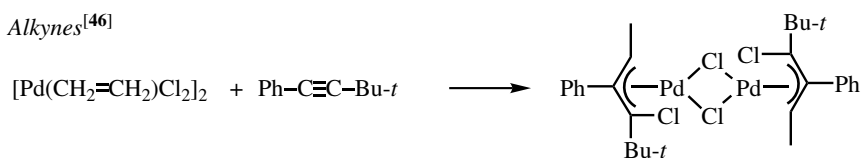
(Scheme 19).^[46]

Tsuji–Trost reaction (**Scheme 20**).^[111]

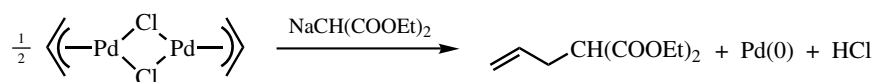
bonylation products (**Scheme 21**).^[112]

actually prepared and isolated (**Scheme 22**).^{[74]–[76]}

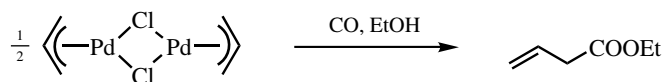
Pd-catalyzed allylation of aldehydes and imines by allylstannane.^[113] This complex has

Allenes^{[103]–[106]}*1,3-Dienes*^{[107]–[109]}*Cyclopropanes*^[110]*Alkynes*^[46]

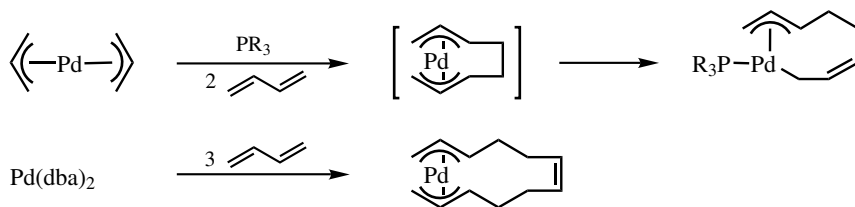
Scheme 19



Scheme 20



Scheme 21



Scheme 22

also been found to react as an amphiphilic allylating agent, that is, a reagent that can simultaneously act as a nucleophile and an electrophile, in the Pd-catalyzed double allylation of activated olefins by allylstannane.^[114]

Like allylic electrophiles, propargylic halides or acetates oxidatively add to Pd(0) derivatives, such as Pd(PPh₃)₄. In this case, however, either η^1 -propargylpalladium or allenylpalladium complexes are obtained depending on the size of the C3 substituent. These complexes display some interesting reactivity.^[115] A recent report clearly demonstrates the possibility of η^3 bonding in the case of propargyl chloride having a bulky group at C3, when the propargylpalladium species is generated from Pd₂(dba)₃ in the presence of 1 equiv of PPh₃ per Pd atom. If a second equivalent of PPh₃ is added, however, the η^1 -propargylpalladium is formed.^[116]

Closely related to the π -allylpalladium complexes are the cyclopentadienylpalladium complexes. Although Cp₂Pd, where Cp is η^5 -C₅H₅, remains unknown, several monocyclopentadienyl-Pd complexes have been prepared and characterized. Some representative examples of such complexes are summarized in **Table 7**.

With the exception of CpPdNO, a Pd(0) species prepared from Pd(Cl)NO and TiCp, all of the Cp-Pd complexes shown in **Table 7** are Pd(II) complexes.

Cyclopentadienylpalladium complexes are generally obtained by the reaction of appropriate Pd complexes with MCp, where M is Na or Tl. Complexes of the CpPd(L)X type, with X = Cl, Br, or I, and L = PR₃, are obtained by the reaction of TiCp or NaCp with dimeric complexes Pd₂X₄L₂ or Pd₂X₂L₂(μ -OAc)₂.^{[119],[127]} These complexes of the general formula CpPd(L)X can in turn react with another ligand L', where L' can be PR₃, CO, or C₂H₄, to give [CpPdLL']X complexes. When X is not a halogen but ClO₄⁻ or PF₆⁻, AgClO₄ or KPF₆, respectively, is required. In special cases where L' = L = PEt₃ or olefin, an alternative synthesis of complexes of the general formula [CpPdL₂]X is possible from X₂PdL₂ and TiCp or FeCpBr(CO)₂. This is the case with [CpPd(PEt₃)₂]Br,^[119] [CpPd(1,5-cod)](FeBr₄),^[120] and [CpPd(η^4 -C₄Ph₄)](FeBr₄).^[120] One such example is shown in **Scheme 23**.

When Pd₂X₂L₂(μ -OAc)₂ is treated with 2 equiv of TiCp per Pd instead of one, (η^5 -Cp)(η^1 -Cp)PdL is obtained.^[123] These complexes exhibit a fluxional behavior in solution, that is, σ/π (or η^1/η^5) exchange of the two Cp ligands.^[123] This is rather interesting, since NMR studies on a variety of Cp-Pd complexes have shown that the Cp ligand is bound symmetrically with no fluxional behavior.^[130]

Other types of cyclopentadienylpalladium complexes have been generated by similar approaches. One such example is CpPd(η^3 -C₃H₅), which is prepared from Pd₂(η^3 -C₃H₅)₂(μ -Cl)₂ (**Scheme 24**).^[118]

Pd complexes containing substituted cyclopentadienyl ligands, such as C₅Me₅ and C₅Ph₅, have also been prepared using various methods discussed above.

Cyclopentadienylpalladium complexes have not yet been shown to be very useful in organic synthesis. This may be due to the fact that the Cp ligand is very labile. It is indeed easily cleaved under a variety of conditions, as exemplified in **Scheme 25**.^[130]

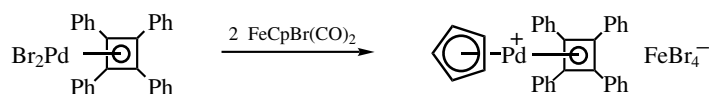
One interesting feature of the Cp-Pd complexes is that they are intensely colored. This characteristic could potentially be interesting, as it provides a direct and straightforward way of monitoring their formation or disappearance.

C.ii. σ -Bonded Complexes: Alkyl, Benzyl, Aryl, Alkenyl, Alkynyl, and Acyl Complexes

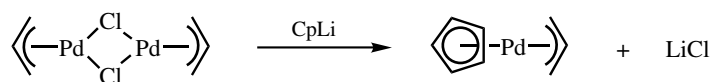
As mentioned previously, σ -bonded organopalladium complexes may contain carbon groups, such as alkyl, benzyl, aryl, alkenyl, alkynyl, and acyl groups. Representative

TABLE 7. Cyclopentadienylpalladium Complexes

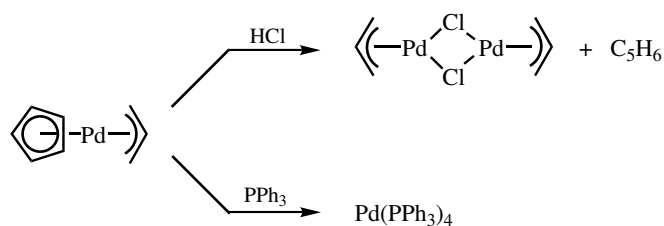
Carbon Number	Pd Complex	Comments	References for Preparation
5			[117]
8			[118]
11		X = Cl, Br, I	[119]
13		X = BF ₄ , FeBr ₄	[120]–[122]
16			[123]
17		X = Br	[119]
23		X = Cl, Br	[119],[124]
24		X = ClO ₄ ; potentially explosive	[125],[126]
25		X = ClO ₄ ; potentially explosive	[125],[126]
28			[127]
			[123]
31		X = PF ₆ , OTf	[128],[129]
33		X = FeBr ₄ , Br; air-stable	[120]



Scheme 23



Scheme 24



Scheme 25

examples of alkyl- and benzylpalladium complexes are listed in **Table 8**. Aryl-, alkenyl-, and alkynylpalladium complexes are exemplified in **Table 9**, and acylpalladium complexes in **Table 10**. In cases where palladium is bonded to chelating ligands, such species may be considered as palladacycles. Those palladacycles containing at least one C—Pd bond in the ring are shown in **Table 11**. Finally, some polymeric carbon—Pd complexes containing Pd in their backbones are given in **Table 12**.

C.ii.a. Alkyl-, Benzyl-, Aryl-, Alkenyl-, and Alkynylpalladium Complexes. Alkyl- and benzylpalladium complexes (**Table 8**) can be obtained by a variety of synthetic methods.

Oxidative addition of Pd(0) species into carbon—halogen bonds leading to monoalkyl- or benzylpalladium complexes of the type “ RPdX ,” where X is a halogen atom, is certainly one of the most general methods for the synthesis of σ -bonded organopalladiums. Pd(0) complexes, such as $\text{Pd}_2(\text{dba})_3$ and $\text{Pd}(\text{PPh}_3)_4$, have been used for this purpose. Metallic palladium generated by metal vapor technique has also been used in the cases of perfluorinated alkyls, such as CF_3I and $\text{CF}_3\text{CF}_2\text{I}$.^[15] Although this method is not widely applicable and is low-yielding, it has been used to generate remarkably stable $\text{CF}_3(\text{CF}_2)_7\text{PdBr}$ (*vide infra*) from the corresponding bromide.^[133] Most often, however, monoalkyl- or benzylpalladium complexes are isolated as complexes of a variety of stabilizing phosphorus or nitrogen ligands and are usually prepared either from a Pd(0) complex of the desired ligand or from $\text{Pd}_2(\text{dba})_3$ in the presence of the desired ligand (**Scheme 26**). Pd(0) complexes can also be generated *in situ* from Pd(II) species in the presence of an appropriate reducing agent (see **Sect. II.2.3**). Unless bidentate ligands are involved, the oxidative addition generally leads to the formation of *trans*-palladium complexes.

Pd(II) complexes can also serve as precursors to monoalkylpalladium complexes via transmetallation if 1 equiv of an organometallic reagent per Pd complex is used. A large

TABLE 8. Alkylpalladium and Benzylpalladium Complexes

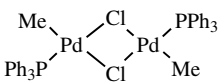
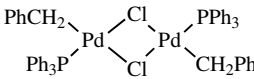
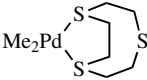
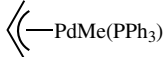
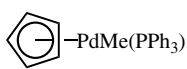
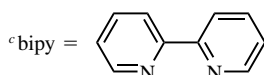
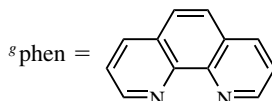
Carbon Number ^a	Pd Complex	Comments	References for Preparation
<i>Monorganyl Complexes</i>			
MONOMERS			
7	MePdI(PMe ₃) ₂	<i>trans</i>	[131],[132]
8	CF ₃ (CF ₂) ₇ PdBr		[133]
9	MePdCl(1,5-cod) ^b		[134]
10	[MePd(PMe ₃) ₃]X	X = BPh ₄	[131],[132]
11	MePdX(bipy) ^c	X = Cl, Br, I	[135],[136]
	MePdI(CNBu- <i>t</i>) ₂	<i>trans</i>	[22]
13	MePdX(PEt ₃) ₂	X = Cl, Br, I; <i>trans</i>	[78],[137]–[139]
	CF ₃ PdBr(PEt ₃) ₂	<i>trans</i>	[15],[140]
	PhCH ₂ PdCl(PMe ₃) ₂	<i>trans</i>	[141]
27	CF ₃ PdI(Ph ₂ PCH ₂ CH ₂ PPh ₂) ^d		[142]
37	MePdX(PPh ₃) ₂	X = Cl, Br, I; <i>trans</i>	[143]–[145]
	CF ₃ PdI(PPh ₃) ₂	<i>trans</i>	[142]
43	PhCH ₂ PdX(PPh ₃) ₂	X = Cl, Br; <i>trans</i>	[144]–[146]
DIMERS			
3	(MePdX·SMe ₂) ₂	X = Cl, Br, I	[147]
19			[134],[148]
25			[149]
<i>Diorganyl Complexes</i>			
MONOMERS			
8			[150]
	Me ₂ Pd(Me ₂ NCH ₂ CH ₂ NMe ₂) ^e		[151]
	Me ₂ Pd(Me ₂ PCH ₂ CH ₂ PMe ₂) ^f		[151]
	Me ₂ Pd(PMe ₃) ₂	<i>cis</i> and <i>trans</i>	[152],[153]
10	Me ₂ Pd(1,5-cod) ^b		[137],[154]
	Et ₂ Pd(PMe ₃) ₂	<i>trans</i>	[153]
12	Me ₂ Pd(bipy) ^c		[135],[137]
14	Me ₂ Pd(phen) ^g		[135]
	Et ₂ Pd(bipy) ^c		[155]
	Me ₂ Pd(PEt ₃) ₂	<i>cis</i> and <i>trans</i>	[137],[153]
22			[156]
24			[157]

TABLE 8. (Continued)

Carbon Number ^a	Pd Complex	Comments	References for Preparation
28	Me ₂ Pd(Ph ₂ PCH ₂ CH ₂ PPh ₂)		[137]
	Me ₂ Pd(PPh ₂ Me) ₂	<i>cis</i> and <i>trans</i>	[158]
38	Me ₂ Pd(PPh ₃) ₂	<i>cis</i> and <i>trans</i>	[137],[158]
46	(<i>neo</i> -pentyl) ₂ Pd(PPh ₃) ₂	<i>cis</i>	[159]

^aNumber of carbons in a monomer unit.^b1,5-cod = 1,5-cyclooctadiene.^dCF₃PdI(dppe).^eMe₂Pd(tmeda).^fMe₂Pd(dmpe).

number of organometallic reagents RM, where M can be Li, Mg, Zn, Cd, Al, Sn, Cu, and so on, can be involved in such transmetallation reactions. This approach generally leads to the formation of the *trans* isomers. Those RM reagents that contain highly electropositive metals (e.g., Li and Mg) tend to introduce two or more R groups into Pd complexes. So, it is often desirable or even necessary to choose more electronegative metals, as in the synthesis of MePdCl(1,5-cod) by the reaction of Cl₂Pd(1,5-cod) with Me₄Sn.^[134]

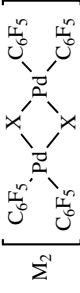
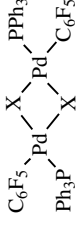
Some of these alkyl- or benzylpalladium derivatives exist as dimers. One interesting group of dimeric alkylpalladium complexes are (MePdX·SMe₂)₂, prepared by the reaction of X₂Pd(SMe₂)₂, where X = Cl, Br, or I, with 1 equiv of MeLi.^[147] The labile SMe₂ ligand can be displaced by a variety of ligands, such as bipy, providing another synthetic route to complexes of the type MePdXL₂ (**Scheme 27**).^{[135],[136]}

Nearly all alkylpalladium complexes that have been isolated are those that do not contain β-hydrogens. This is because those containing β-hydrogens undergo rapid β-elimination to give alkenes and HPdX. This process involving *syn* β-elimination is a crucial step in the Pd-catalyzed Heck reaction.^{[160],[161]} Perfluoroalkylpalladium halides are by far more stable than the corresponding ordinary alkylpalladium halides. For example, CF₃CF₂PdI is stable at room temperature.^[15]

Dialkylpalladium complexes are typically obtained by the reaction of Pd(II) species with alkylmetal reagents. While the *cis* isomers are obtained by the treatment of X₂PdL₂ (X = Cl or Br) with alkyllithium or -magnesium reagents (**Scheme 28**),^[137] the reaction of Pd(acac)₂ with AlR₂(OEt) or Al₂R₃(OEt)₃, in the presence of the desired ligand, is a well-established route to *trans*-R₂PdL₂.^[153] Alternatively, *trans* dialkylpalladium complexes can be obtained by the reaction of preformed *trans*-RPdXL₂ with an organometallic reagent (**Scheme 28**).^[158]

The stepwise approach shown in **Scheme 28** provides a convenient route to diorganypalladium complexes containing two different carbon groups, such as (η⁵-C₅H₅)PdMe(PPh₃), formed by the reaction of MeMgBr with (η⁵-C₅H₅)PdBr(PPh₃).^[157] It should be noted,

TABLE 9. Aryl-, Alkenyl-, and Alkynyl/palladium Complexes

Carbon Number ^a	Pd Complex	Comments	References for Preparation
<i>Monorganyl Complexes</i>			
MONOMERS			
12	PhPdI(Me ₂ NCH ₂ CH ₂ NNMe ₂) ^b PhPdI(PMe ₃) ₂	<i>trans</i>	[163] [131],[132]
14	(C ₆ F ₅)PdCl(1,5-cod) ^c	X = Cl, Br, I; <i>trans</i>	[164]
18	PhPdX(PEt ₃) ₂		[73],[137], [143],[165]
28	(CH ₂ =CH)PdBr(PPh ₂ Me) ₂	<i>trans</i>	[166]
40	(Ph ₂ C=CH)PdBr(PPh ₂ Me) ₂	<i>trans</i>	[166]
42	PhPdX(PPh ₃) ₂ (C ₆ F ₅)PdCl(PPh ₃) ₂	X = Cl, Br, I; <i>trans</i>	[143],[167]–[170] [171]
43	<i>p</i> -NO ₂ (C ₆ H ₄)PdI(PPh ₃) ₂	<i>trans</i>	[169]
44	[(C ₆ F ₅)Pd(CO)(PPh ₃) ₂] _n (PhCH=CH)PdBr(PPh ₃) ₂ (PhC≡C)PdCl(PPh ₃) ₂	X = ClO ₄ <i>trans</i> ; <i>E</i> and <i>Z</i> isomers <i>trans</i>	[172] [173] [174]
DIMERS AND POLYMERS			
6	M ₂ [(C ₆ X ₅)PdBr ₂] ₂ [(C ₆ F ₅)PdX] _n	X = F, Cl; M = Bu ₄ N X = Cl, Br	[175] [15],[176]
12	M ₂ 	X = Cl, Br; M = Bu ₄ N	[177]
24		X = Cl, Br, I	[171],[178]

Bis-, Tris-, and Tetrakisorganyl Complexes

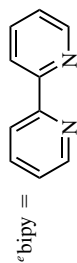
MONOMERS			
8	$K_2Pd(C\equiv CH)_4$		[179]
10	$(HC\equiv C)_2Pd(PMe_3)_2$	<i>trans</i>	[180],[181]
14	$(C_6X_5)_2Pd(CO)_2$	X = F, Cl; <i>cis</i>	[182]
20	$(C_6X_5)_2Pd(THF)_2^d$	X = F, Cl; <i>cis</i>	[182]
	$(C_6F_5)_2Pd(1,5-cod)^c$		[183],[184]
22	$(C_6F_5)_2Pd(bipy)^e$		[185]
24	$Li_2Pd(C\equiv CBut)_4$		[186]
	$Ph_2Pd(PEt_3)_2$	<i>trans</i>	[137],[187]
	$M_2Pd(C_6F_5)_4$	M = K, Bu ₄ N	[177],[188]
26	$(t-BuCH=CH)_2Pd(PEt_3)_2$	<i>trans</i> ; <i>E</i> isomer	[187]
30	$Ph[Me(CH_2)_3CH=CH](PEt_3)_2$	<i>trans</i> ; <i>E</i> isomer	[187]
32	$(HC\equiv C)_2Pd(dppe)^f$		[179]
	$K_2Pd(C\equiv CPh)_4$		[179]
	$(MeC\equiv C)_2Pd(dppe)^f$		[179]
42	$(PhC\equiv C)_2Pd(dppe)^f$		[179]
48	$(C_6F_5)_2Pd(PPh_3)_2$	<i>cis/trans</i> mixture	[178]
52	$(PhC\equiv C)_2Pd(PPh_3)_2$	<i>trans</i>	[189],[190]

^aNumber of carbons in a monomer unit.

^bPhPd(Imeda).

^c1,5-cod = 1,5-cyclooctadiene.

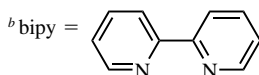
^dTHF = Tetrahydrofuran.



^fdppe = Ph₂PCH₂CH₂PPh₂.

TABLE 10. Acylpalladium and α -Functionalized Organylpalladium Complexes

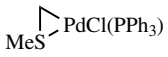
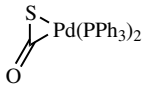
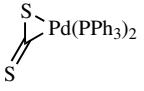
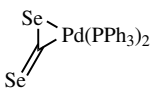
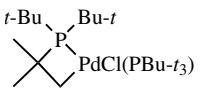
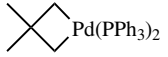
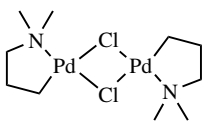
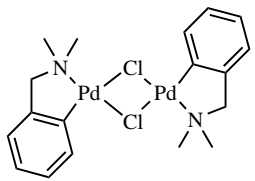
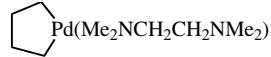
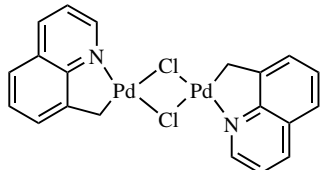
Carbon Number ^a	Pd Complex	Comments	References for Preparation
<i>Monoacyl Complexes</i>			
MONOMERS			
8	MeCOPdI(PMe ₃) ₂	<i>trans</i>	[131],[132]
11	[MeCOPd(PMe ₃) ₃]BPh ₄		[131],[132]
14	[PhCOPd(PMe ₃) ₂ (CO)]BF ₄	<i>trans</i> ; stable under CO	[203]
	PhCH ₂ COPdCl(PMe ₃) ₂	<i>trans</i>	[141]
	MeCOPdCl(PEt ₃) ₂	<i>trans</i>	[134],[138]
16	[PhCOPd(PMe ₃) ₃]BPh ₄		[131],[132]
38	MeCOPdX(PPh ₃) ₂	X = Cl, I; <i>trans</i>	[169],[204]
	MeOOCpdCl(PPh ₃) ₂	<i>trans</i>	[205]
	MeSCH ₂ PdCl(PPh ₃) ₂	<i>trans</i>	[206]
	NCCH ₂ PdCl(PPh ₃) ₂	<i>trans</i>	[207]
43	PhCOPdX(PPh ₃) ₂	X = Cl, Br, I; <i>trans</i>	[169],[208],[209]
44	PhCH ₂ COPdBr(PPh ₃) ₂	<i>trans</i>	[169],[208]
	PhCOCOPdCl(PPh ₃) ₂	<i>trans</i>	[210]
DIMERS			
8	[MeCOPdCl(PEt ₃)] ₂		[138]
25	[PhCOPdI(PPh ₃)] ₂		[211]
<i>Bis-, Tris-, and Tetrakisacyl Complexes</i>			
MONOMERS			
14	(MeOOC) ₂ Pd(bipy) ^b		[212]
20	[(MeOOC) ₂ CH] ₂ Pd(bipy) ^b		[213]
40	(MeOOC) ₂ Pd(PPh ₃) ₂	<i>trans</i>	[214]

^aNumber of carbons in a monomers unit.

however, that the reaction of preformed PhCH₂PdX(PPh₃)₂, where X = Cl or Br, with Me₄Sn or MeMgBr does not give the expected (PhCH₂)MePd(PPh₃)₂ but leads, instead, to the formation of MePdX(PPh₃)₂ via carbon-for-carbon transmetallation.^[144] Under catalytic conditions, however, the desired transmetallation does take place.^{[144],[145]}

Along with the previously mentioned β -elimination reaction, dialkylpalladium complexes can undergo reductive elimination. Here again, perfluorination tends to inhibit the process. Evidently, the σ -donating ability of the carbon group seems to promote reductive elimination. Additional requirements must be met for reductive elimination to take place, the most crucial one being the *cis* arrangement of the two alkyl groups.^[158] This condition is necessary but not sufficient. Thermal decomposition of Et₂Pd(bipy), for instance, gives ethene and ethane via β -elimination but no butane, despite the favorable *cis* arrangement of the two ethyl groups. In the presence of methyl acrylate, however, butane is obtained in high yields.^[155] The effect of methyl acrylate is explained in terms of complexation of the 16-electron Et₂Pd(bipy), which plugs the available empty orbital necessary for

TABLE 11. Palladacycles Containing One or Two Ring C—Pd σ -Bonds

Carbon Number ^a	Pd Complex	Comments	References for Preparation
THREE-MEMBERED RINGS			
20			[206]
37			[218]
			[219]
			[220]
FOUR-MEMBERED RINGS			
24			[221]
41			[159]
FIVE-MEMBERED RINGS			
5			[222]
9		Commercially available	[223]
10		(CH ₂) ₄ Pd(tmeda)	[224]
			[225]

(Continued)

TABLE 11. (Continued)

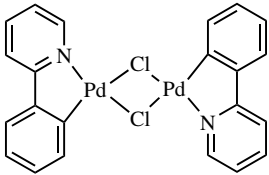
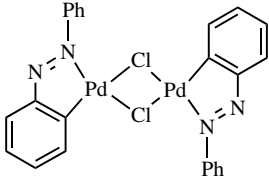
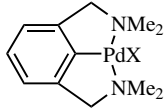
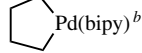
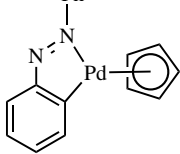
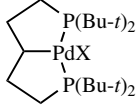
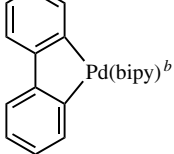
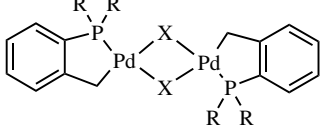
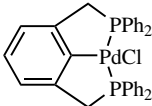
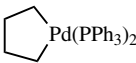
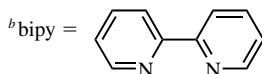
Carbon Number ^a	Pd Complex	Comments	References for Preparation
11			[226]
12			[227]
		X = Cl, Br, I	[228]
14			[224]
17			[229]
21–22		X = Cl, H, Me	[230],[231]
22			[232]
23		X = OAc; R = o-tolyl; commercially available	[233]

TABLE 11. (Continued)

Carbon Number ^a	Pd Complex	Comments	References for Preparation
32			[234]
40			[224]

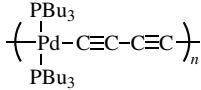
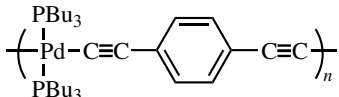
^aNumber of carbons in a monomer unit.

β -elimination. The nature of the ligand can also affect the course of the thermal decomposition of dialkylpalladium complexes. In cross-coupling reactions, for instance, chelating ligands have been found to favor the desired reductive elimination.^[162]

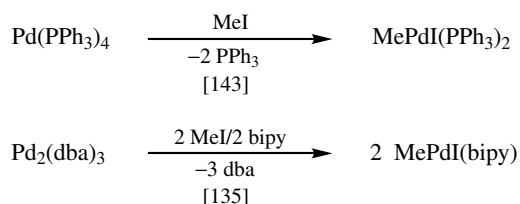
Aryl-, alkenyl-, and alkynylpalladium complexes (**Table 9**) are generated in manners similar to the preparation of alkyl- and benzylpalladium derivatives. However, oxidative addition is much more widely applicable and satisfactory than in the preparation of alkylpalladium derivatives, since aryl, alkenyl, and alkynyl halides are not only much more reactive toward Pd(0) complexes than their alkyl counterparts but are also uncomplicated by β -elimination.

While oxidative addition appears to be the method of choice for preparing *trans* monoorganypalladium complexes containing an aryl, alkenyl, or alkynyl group, transmetallation with an organometal containing Li, Na, Mg, Zn, Hg, or Sn provides a general route to diorganypalladium complexes. For the preparation of alkynyl-Pd complexes, alkynylcopper reagents generated *in situ* from terminal alkynes have been used.^{[180],[181]} The *trans* diorganypalladium derivatives are usually obtained unless a bidentate ligand is used.

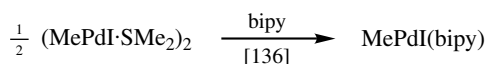
TABLE 12. Polymers Containing Palladium in the Polymer Backbones

Carbon Number ^a	Pd Complex	References for Preparation
28		[241]
34		[242]

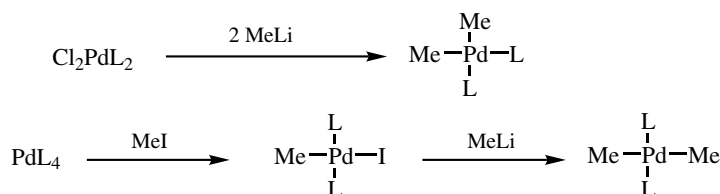
^aNumber of carbons in a monomer unit.



Scheme 26



Scheme 27

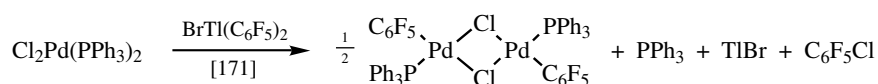


Scheme 28

Oxidative addition requires either the use or the *in situ* generation of a Pd(0) complex. Metal vapor techniques, for instance, have allowed the preparation of nonligated polymeric aryl–Pd complexes, $(\text{C}_6\text{F}_5\text{PdX})_n$, where $\text{X} = \text{Cl}$ or Br .^[15] The higher thermal stability of the perfluoroorganylpalladium complexes as compared with their ordinary organopalladium derivatives^[191] is once again clearly indicated (*vide infra*).

Although a wide variety of leaving groups including I, Br, Cl, and various oxy groups have been employed in oxidative addition, it completely fails to work with organic fluorides. Recently, however, $\text{MePdF(PPh}_3)_2$ and $\text{PhPdF(PPh}_3)_2$ have been obtained by sonication of the corresponding iodide in the presence of AgF .^[192]

Monoarylpalladium complexes have also been prepared by transmetallation. For example, $\text{PhPdCl(PEt}_3)_2$ and $\text{PhPdBr(PEt}_3)_2$ have been prepared by the reaction of Ph_2Hg and PhMgBr with $\text{Cl}_2\text{Pd(PEt}_3)_2$ and $\text{Br}_2\text{Pd(PEt}_3)_2$, respectively.^{[137],[165]} On the other hand, dimeric $[(\text{C}_6\text{F}_5)\text{PdCl(PPh}_3)_2]_2$ has been obtained from $\text{Cl}_2\text{Pd(PPh}_3)_2$ and $\text{TlBr(C}_6\text{F}_5)_2$ (Scheme 29).^[171]



Scheme 29

Redistribution reactions between two palladium complexes have also proved useful for the generation of monoarylpalladium species. For example, $\text{C}_6\text{F}_5\text{PdCl}(1,5\text{-cod})$ is obtained from $(\text{C}_6\text{F}_5)_2\text{Pd}(\text{THF})_2$, $\text{Cl}_2\text{Pd}(\text{PhCN})_2$, and 1,5-cyclooctadiene (**Scheme 30**).^[164]



Scheme 30

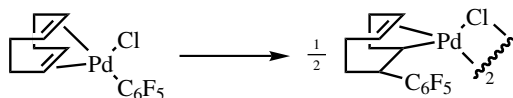
Transmetalation of preformed RPdXL_2 , such as $\text{PhPdI}(\text{PEt}_3)_2$, allows the formation of *trans* diorganylpalladium complexes having two different organic groups, such as $\text{Ph}(E)\text{-Me}(\text{CH}_2)_5\text{CH=CHPd}(\text{PEt}_3)_2$ or $\text{Ph}(\text{Me})\text{Pd}(\text{PEt}_3)_2$.^[187] This process is a crucial step in the Pd-catalyzed cross-coupling reactions.

Although most of the diorganylpalladium complexes of nonchelating ligands are *trans*, some synthetic routes to *cis* diorganylpalladium complexes, such as *cis*-(C_6F_5)₂ $\text{Pd}(\text{THF})_2$ and *cis*-(C_6F_5)₂ $\text{Pd}(\text{CO})_2$, exist. While *cis*-(C_6F_5)₂ $\text{Pd}(\text{THF})_2$ can be obtained from $(\text{Bu}_4\text{N})_2[(\text{C}_6\text{F}_5)_2\text{PdCl}]_2$, *cis*-(C_6F_5)₂ $\text{Pd}(\text{CO})_2$ is obtained from the corresponding THF complex via displacement of THF.^[184] The starting $(\text{Bu}_4\text{N})_2[(\text{C}_6\text{F}_5)_2\text{PdCl}]_2$ is in turn obtained from $(\text{Bu}_4\text{N})_2(\text{Pd}_2\text{Cl}_6)$ and $(\text{C}_6\text{F}_5)\text{MgBr}$.^[177]

It is interesting to note that homoleptic tetraaryl- and tetraalkynylpalladium “ate” complexes have been obtained by the reaction of K_2PdCl_4 or $\text{Cl}_2\text{Pd}(\text{PPh}_3)_2$ with aryl- or alkynyllithium reagents.^{[186],[188]} These tetraorganopalladate complexes do not readily undergo reductive elimination, providing a mechanistic interpretation of the inhibitory action of highly electropositive metals, such as Li, in some Pd-catalyzed coupling reactions.^[186]

Also interesting is the preparation of cationic palladium complexes, such as $[\text{MePd}(\text{PMe}_3)_2]\text{X}^{[132]}$ and $[(\text{C}_6\text{F}_5)\text{Pd}(\text{CO})(\text{PPh}_3)]\text{X}$,^[172] considering the fact that cationic palladium complexes are believed to be the actual catalytic species in several Pd-catalyzed processes, an example of which being the copolymerization of alkenes and CO.^[16]

The reactivity of the C—Pd bond is very diverse. In addition to the previously discussed β -elimination and reductive elimination, alkyl-, benzyl-, aryl-, alkenyl-, and alkynyl-Pd complexes can undergo *syn* addition of the C—Pd bond across the C—C bond of alkenes and alkynes, that is, carbopalladation. This reaction can generate alkyl- or alkenyl-Pd complexes and is occasionally used as a preparative method, as exemplified in **Scheme 31**.^[164] Closely related is the hydropalladation of alkenes and alkynes. However, these processes are mostly observed under catalytic conditions.^[193]



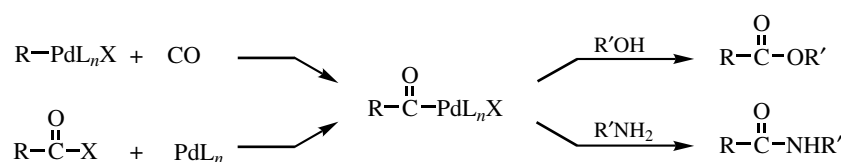
Scheme 31

A wide variety of nucleophiles, such as KCN ,^[194] amines,^[195] alkoxides,^{[195],[196]} or sulfides,^[197] can react with monoarylpalladium complexes, to give RCN , RNR'_2 , ROR' , or RSR' . In these processes, the formation of a C—Nu bond is thought to occur via reductive

elimination of a RPdNu intermediate. As in the C—C bond-forming reductive elimination, judicious choice of ligands is crucial in favoring the desired process over the competing side reactions, such as β -H elimination.^[198] Although less effective and hence rarely used, C—Pd bonds can also be cleaved with electrophiles, such as HCl or Br_2 , to give RH or RBr .^[199]

It is worth noting that alkyl- and arylpalladium complexes containing aryl phosphines can undergo alkyl-aryl and aryl-aryl exchange between Pd and P, which can proceed via phosphine dissociation followed by oxidative addition.^{[200]–[202]}

C.ii.b. Acylpalladium Complexes. Among the reaction paths that C—Pd bonds can undergo, CO insertion (**Scheme 32**) is of great importance in many catalytic processes. This reaction has been used to generate a number of acyl-Pd complexes (**Table 10**).



Scheme 32

Carbon monoxide can easily insert itself into various C—Pd bonds containing alkyl, benzyl, aryl, alkenyl, alkynyl, and others. The resulting acyl—Pd bond is less prone to insert CO, which explains why products of double carbonylation are rare even under catalytic conditions. Acyl—Pd complexes are also accessible via oxidative addition of $\text{Pd}(0)$ into acyl halides (**Scheme 32**).^{[131],[132],[209],[210]} In fact, the generation of $\text{PhCO-COPdCl(PPh}_3)_2$ from PhCOCOC and $\text{Pd(PPh}_3)_4$ has been claimed.^[210] Most of the Pd-catalyzed double carbonylation reactions (**Sect. VI.2.1.4**) involve reductive elimination of bis(acyl)palladium derivatives,^[215] as exemplified by an efficient synthesis of pyridylglyoxylic amides and esters.^[216] As a rule, acylpalladium derivatives of the type RCOCOPdL_n are prone to facile decarbonylation and hence too unstable to serve as synthetically useful intermediates.^[210] Acylpalladium derivatives undergo a wide variety of reactions including solvolysis shown in **Scheme 32**.^[216] These and other reactions of acylpalladium derivatives are discussed mainly in **Parts VI** and **VIII**.

Related alkoxy carbonyl—Pd complexes of the type $(\text{ROOC})\text{PdClL}_2$ or $(\text{ROOC})_2\text{PdL}_2$ are typically generated from Cl_2PdL_2 , CO, and LiOR . Attack by alkoxy anions on the coordinated CO can explain the process. However, insertion of CO into the Pd—OR bond is a possible alternative. In fact, NMR spectroscopy has provided some evidence for the formation of $(\text{MeO})_2\text{Pd(bipy)}$ during the preparation of $(\text{MeOOC})_2\text{Pd(bipy)}$.^[212]

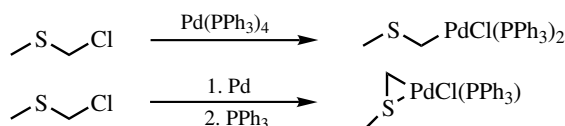
Also related to the acyl—Pd complexes are the iminoacyl—Pd complexes and the complexes containing a heteroatom in the α position, for example, $\text{MeSCH}_2\text{PdCl(PPh}_3)_2$. While the iminoacyl complexes are obtained similarly to their acyl analogs by insertion of isonitriles into the C—Pd bond,^[22] the α -heterofunctional complexes are obtained in manners similar to the synthesis of alkyl—Pd complexes via oxidative addition or transmetalation. One notable difference between insertion of CO and that of isonitriles is that the latter can lead to multiple insertion.^[217]

Other CO-containing organopalladium derivatives in which the CO group is not directly bonded to Pd are also known and implicated as transient intermediates (**Part VI**). Some such compounds have also been prepared as discrete species, as exemplified by

$[(\text{COOMe})_2\text{CH}_2]_2\text{Pd}(\text{bipy})$ generated by the reaction of $(\text{COOMe})_2\text{CH}_2\text{Na}$ with $\text{Cl}_2\text{Pd}(\text{bipy})$.^[213]

C.ii.c. Palladacycles. Various reactions discussed in this section can also take place intramolecularly to produce palladacycles containing one or two ring C—Pd bonds (**Table 11**). Palladacycles of various ring sizes have been generated and isolated. Even so, the great majority of palladacycles are five-membered.

As in the other cases, oxidative addition and transmetalation are two main routes to palladacycles. Some representative examples follow. Oxidative addition of Pd into the C—Cl bond of MeSCH_2Cl in the presence of 1 equiv of PPh_3 gives a three-membered palladacycle.^[206] In the presence of 2 equiv or more of PPh_3 an acyclic species is formed (**Scheme 33**).^[206] The reaction of $\text{Cl}_2\text{Pd}(\text{PPh}_3)_2$ with $\text{Li}(\text{CH}_2)_4\text{Li}$ produces $(\text{CH}_2)_4\text{Pd}(\text{PPh}_3)_2$.^[224]



Scheme 33

Palladacycles can, however, be generated by other reactions as well. For instance, three-membered palladacycles have been obtained by complexation of $\text{Pd}(0)$ species with heteroatom containing π -compounds such as COS , CS_2 , and CSe_2 . As π -complexation can alternatively be viewed as an oxidative complexation (**Sect. II.3.1**), these palladium complexes can be viewed either as η^2 complexes or as three-membered palladacycles (**Table 11**).

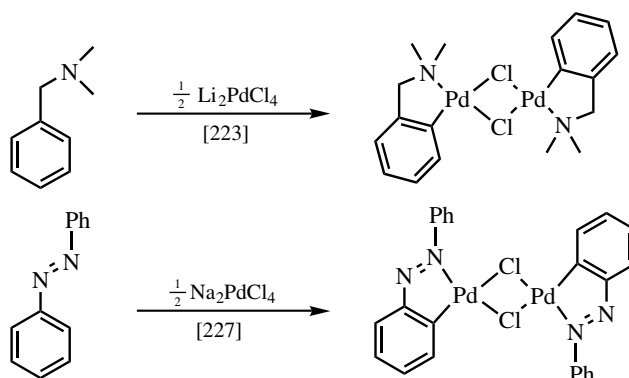
One widely observable reaction for the preparation of five-membered palladacycles is intramolecular C—H activation assisted by a donor atom, termed cyclopalladation or orthopalladation. Notably, the reaction of PdCl_2 or M_2PdCl_4 ($\text{M} = \text{Li}$ or Na) with functionalized arenes, such as *N,N*-dimethylbenzylamine or azobenzene, gives the corresponding five-membered palladacycles as the *trans* chlorine-bridged dimers in most cases (**Scheme 34**). A competitive experiment has shown that the former substrate is a better ligand for Pd than the latter.^[223] Furthermore, only tertiary benzylamines were found to be capable of participating in these reactions.^[223] In the cases of the primary and secondary benzylamines, their interaction with Pd can lead to tighter amine—Pd complexes that are not sufficiently reactive for C—H activation.

2-Phenylpyridine and *P,P*-disubstitutedbenzylphosphines can also participate in cyclometallation reactions leading to five-membered palladacycles, as shown in **Table 11**. Oxygen and sulfur analogs have also been used.

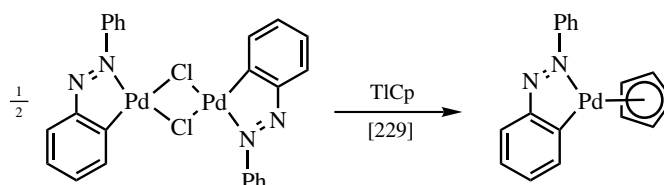
Halogen-bridged dimeric palladacycles can serve as precursors to monomeric derivatives that can readily be obtained by treating the dimers with various reagents, such as phosphines and organometals (**Scheme 35**).

Benzylic C—H activation can also occur readily to give five-membered palladacycles containing $\text{Pd—C}_{\text{sp}^3}$ bonds (**Scheme 36**). Five-membered palladacycles containing $\text{Pd—C}_{\text{sp}^3}$ bonds may also be prepared via transmetalation (**Scheme 36**).

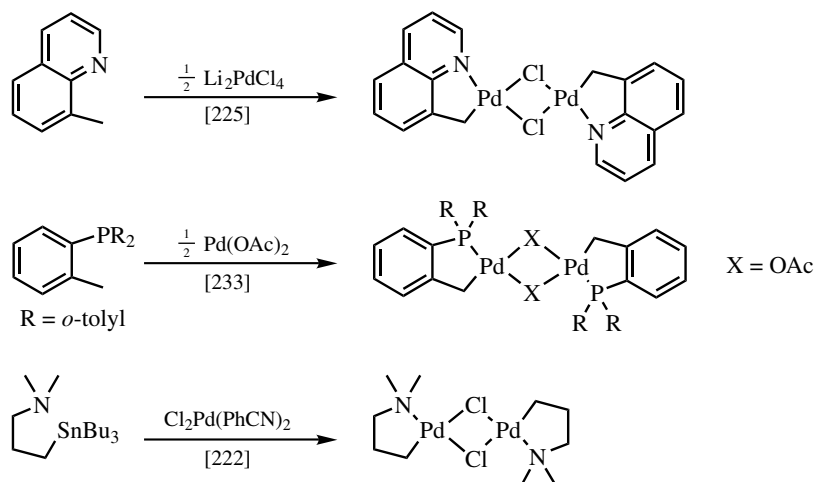
Palladacycles containing C—Pd σ -bonds can exhibit similar reactivity patterns as usual C—Pd containing complexes, but chelation usually confers enhanced levels of stability to palladacycles. One representative class of reactions that palladacycles undergo is



Scheme 34



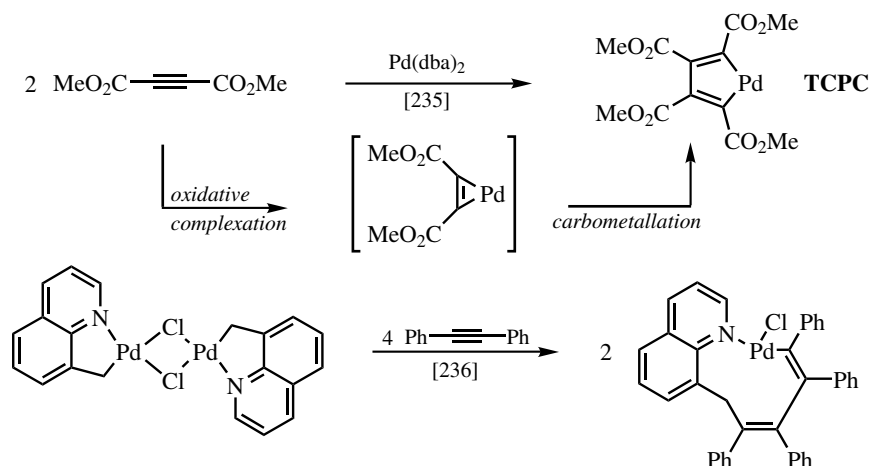
Scheme 35



Scheme 36

ring expansion via carbopalladation, which, in turn, generates new palladacycles (**Scheme 37**).^{[235],[236]} Double insertion has also been observed (**Scheme 37**).^[236] Conversion of TCPC, which is generated as a tetramer, into monomeric TCPC(L₂) can be achieved by its complexation with a variety of ligands.^{[237],[238]}

Palladacycles have also proved to be useful as catalysts for several organic transformations. For instance, TCPC derivatives have been widely used for enyne metatheses and

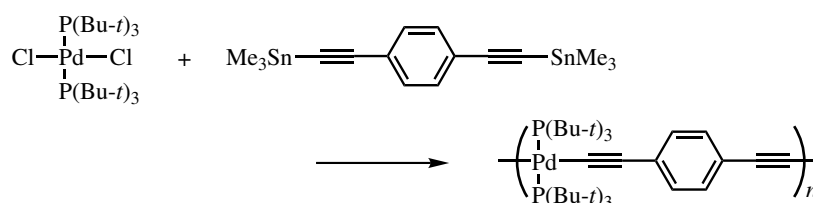


Scheme 37

cyclization reactions,^[64] and commercially available *trans*-di(μ -acetato)bis[*o*-(di-*o*-tolylphosphine)benzyl]dipalladium has been found to be an efficient catalyst for the Heck olefination^[233] and the Suzuki coupling^[239] of chloro- and bromoarenes. Similarly, an orthopalladated triarylphosphite complex obtained by the cyclometallation of tris(2,4-di-*t*-butylphenyl)phosphite with PdCl_2 was recently found to be an active catalyst for the synthesis of biaryls derivatives by the Suzuki reaction.^[240]

C.ii.d. Polymers Containing C—Pd Bonds in the Polymer Backbone. Some examples of polymers containing C—Pd bonds in their backbones are known, as indicated in **Table 12**.

These polymers are synthesized in ways similar to the preparation of alkynylpalladium complexes from Pd(II) species and alkynylmetals, such as alkynyltins and alkynylcoppers (**Scheme 38**).^[241] Concentrated solutions of these polymers have been found to form lyotropic liquid crystals.^{[241],[243]}



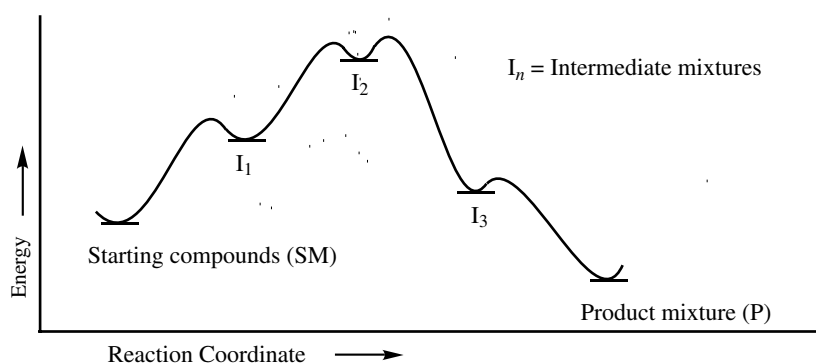
Scheme 38

D. CONCLUSION

1. Various methods of generation of organopalladium derivatives discussed in **Sects. I.2** and **II.3.1** are also applicable to the syntheses of discrete organopalladium compounds that can be isolated and identified. In most of the catalytic reactions, their formation is assumed, and their stoichiometric preparation discussed in this section lends strong support for such assumptions. So the stoichiometric preparation of

organopalladium compounds provides the foundation for structural and mechanistic investigations of organopalladium chemistry.

2. A statement of caution is in order. In the stoichiometric synthesis of organopalladium complexes, the formation of organopalladium complexes themselves must be thermodynamically favorable. On the other hand, their formation need not be thermodynamically favorable in their catalytic reactions, since the only two critical requirements in catalytic processes are that the overall stoichiometric transformation be thermodynamically favorable and that each and every catalytic microstep be kinetically favorable. Thus, so long as the kinetic requirement is met, even thermodynamically unfavorable catalytic microsteps, be they oxidative addition, transmetallation, or reductive elimination, can be segments of catalytic processes. Oxidative addition of allyl acetates with $\text{Pd}(\text{PPh}_3)_4$ in the Tsuji–Trost reaction and some transmetallation processes in the Pd-catalyzed cross-coupling are likely to be thermodynamically unfavorable. This significant difference indicated in a generalized manner in **Scheme 39** should always be kept in mind. For example, the oxidative addition step in a catalytic reaction may be represented by the $\text{SM} \rightarrow \text{I}_1$ process, which is indicated as a thermodynamically unfavorable step.



Scheme 39

3. Organopalladium compounds prepared as discussed in this section can also serve as catalysts or catalyst precursors. Further investigations along this line will undoubtedly broaden the scope and applicability of the Pd catalysis in organic synthesis.

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