Pd–L*

II.2.7 Chiral Pd(0) and Pd(II) Complexes

MASAMICHI OGASAWARA and TAMIO HAYASHI

A. INTRODUCTION

Among a numerous number of chiral palladium complexes, those applied to organic synthesis, either catalytically or stoichiometrically, will be a central subject of this section. This section will cover only the chiral palladium complexes whose X-ray crystal structures and/or NMR data have been reported. Thus, chiral palladium catalysts that are generated *in situ* in the reaction media are excluded from discussion. Because of recent progress of the X-ray crystallographic and NMR techniques/instruments, examples of well-characterized chiral palladium species are growing rapidly.

Zero- and divalent palladium species possess d^{10} and d^8 configurations respectively. Pd(II) species prefer low-spin (diamagnetic) forms to high-spin (paramagnetic) forms, and thus they are NMR active. In accordance with this, the ideal geometry at the palladium centers in the four-coordinate Pd(II) complexes is square planar. The fifth d orbital ($d_{x^2-y^2}$ orbital) is too high in energy to be accessed as the fifth coordination site in these square planar complexes. For this reason, the Pd(II) species tend to have a 16-electron count rather than an 18-electron count. On the other hand, Pd(0) prefers a four-coordinate 18-electron form with tetrahedral geometry, though three-coordinate 16-electron, or two-coordinate 14-electron species are also known with certain steric protection from the coordinating ligands.

B. *IN SITU* GENERATION OF CHIRAL PALLADIUM COMPLEXES

Since palladium is an expensive noble metal, palladium species have mainly been employed as catalysts in organic synthesis and examples of stoichiometric applications are relatively few. In many synthetically useful Pd-catalyzed reactions, palladium species interconvert their oxidation states between Pd(0) and Pd(II) in the catalytic cycles. For these catalytic reactions, both appropriate Pd(0) and Pd(II) species work similarly well as catalyst precursors. Among the examples of these reactions are the Heck reaction, π-allylpalladium-mediated reactions, and cross-coupling. This concept is illustrated in **Scheme 1**. Most of these Pd-catalyzed reactions have been extended to their asymmetric counterparts by employing chirally modified palladium complexes. In general, these chiral palladium catalysts are generated in the reaction solution from appropriate palladium

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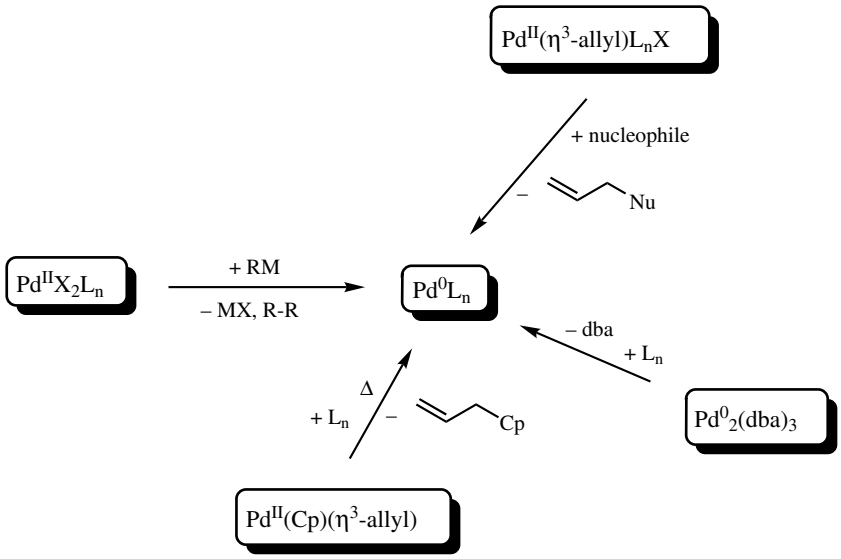


Scheme 1

precursors and chiral ligands. These *in situ* generated Pd species show comparable catalytic activity and stereoselectivity with the corresponding isolated complexes. This is the great advantage of palladium chemistry; tedious isolation and purification of the catalysts can be avoided prior to the catalytic reactions. In this section, frequently employed palladium precursors will be briefly described.

$Pd_2(dba)_3 \cdot CHCl_3$. This is the most frequently employed precursor to a variety of chiral Pd(0) complexes. A chloroform molecule is cocrystallizing with the binuclear palladium moiety par unit. A number of variants with different cocrystallized solvents are known and show similar reactivity with the chloroform adduct, which includes dba (dibenzalacetone) cocrystals [i.e., $Pd_2(dba)_3 \cdot (dba)$]. This species is often referred as $Pd_2(dba)_4$ or $Pd(dba)_2$. In the presence of stronger ligands, such as phosphines, dba ligands in the complex are easily replaced to give new palladium species. In many cases, the released dibenzalacetone is difficult to remove and remains in the reaction mixture. Sometimes, the remaining dibenzalacetone works as an inhibitor; thus, special attention must be paid to the dba.

$Pd(\eta^3\text{-}allyl)(\eta^5\text{-}C_5H_5)$. This Pd(II) species is the precursor to Pd(0) complexes. The coordinating ligands, allyl and Cp, thermally dissociate from the palladium center in a fashion of reductive elimination to generate new Pd(0) species in the presence of external ligands. Although this complex is a cleaner source for Pd(0) than the Pd-dba species (the by-product, allylcyclopentadiene, is easier to remove and less reactive than dba), thermal instability and handling difficulty limit applications of this species.

$PdCl_2(cod)$, $PdCl_2(MeCN)_2$, and $PdCl_2(PhCN)_2$. Inorganic palladium dichloride, $PdCl_2$, possesses polymeric structure. Thus, it is virtually insoluble in organic solvent and is inappropriate as a direct precursor to divalent palladium reagents. All three complexes

represented here possess weakly coordinating ligands such as cyclooctadiene (cod) or nitriles, which are easily replaced by stronger ligands. They are easily prepared from palladium dichloride; thus, these palladium complexes are good sources for a variety of dichloropalladium complexes.

$[PdCl(\eta^3\text{-}C_3H_5)]_2$. Two bridging chloride–palladium bonds in the complex are easily broken in the presence of external ligands L to give new complexes of the type either $PdCl(\eta^3\text{-}C_3H_5)(L)$ or $[Pd(\eta^3\text{-}C_3H_5)(L)_2]Cl$. Since divalent d^8 palladium species tend to possess a 16-electron count, the latter ionic form is preferred with 2 equiv (to Pd) of monodentate ligand or with a bidentate ligand. The newly formed π-allylpalladium complexes react with appropriate nucleophiles Nu^- to give allyl–Nu and new Pd(0) species in solution. Thus, these π-allylpalladium complexes can serve as potential Pd(0) sources.

$[Pd(MeCN)_4](BF_4)_2$. As is the case with $PdCl_2(MeCN)_2$ explained above, the coordinating acetonitriles in this cationic complex are also weakly coordinating and easily replaced by external ligands. With 1 equiv of bidentate ligand (many chiral ligands are bidentate), only two of the four acetonitrile ligands are substituted, and the remaining two coordinating acetonitriles can serve as a potential vacant site (reactive site) at the palladium center in the catalytic reactions.

$Pd(OAc)_2$. Palladium(II) acetate can be a source of Pd(0) complexes. Since it can easily be reduced to zerovalent palladium by appropriate reductants, the new Pd(0) complexes are generated in the presence of suitable ligands. In many situations, solvent (alcohol, etc.) or coexistent ligands (such as phosphines) work as reductants; thus, additional reducing reagents are not always required.

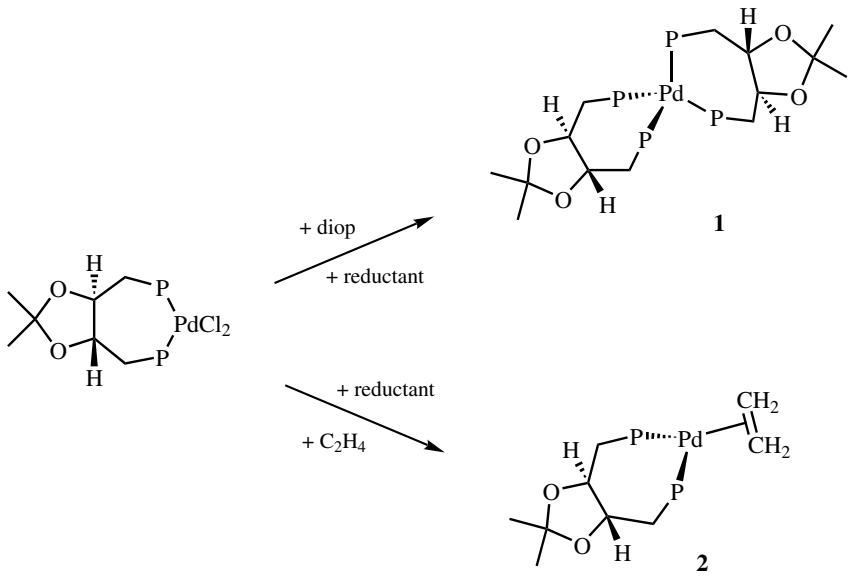
$Pd(PPh_3)_4$. In this complex, four relatively bulky ligands coordinate to the same metal center. Because of the steric congestion, the coordinating PPh_3 tends to dissociate in solution. This behavior can be attributed to the high catalytic activity of this species. Meanwhile, in the presence of stronger donors than PPh_3, the PPh_3 ligands are substituted with the external ligands. With the multidentate incoming ligands, the chelating effect also assists the substitution. By employing appropriate chiral ligands, new chiral palladium complexes can be generated from $Pd(PPh_3)_4$. For example, $Pd(PPh_3)_4$ reacts with excess DIOP to give $Pd(diop)_2$ and free PPh_3.[1] The dissociated PPh_3, which is achiral phosphine, has negative effects in terms of stereoselectivity in the catalytic asymmetric reactions; thus, this method has rarely been examined lately, especially after discovery of the other precursors to Pd(0) species.

C. ZEROVALENT CHIRAL PALLADIUM COMPLEXES

Examples of well-characterized isolated chiral complexes of Pd(0) are very rare. As explained earlier, both appropriate Pd(0) and Pd(II) precursors generate identical catalytically active species in the course of the reactions. In general, the Pd(II) species are more tolerant to air than the Pd(0) complexes and are easier to handle. For this reason, the Pd(II) precursors are preferred to the Pd(0) species for most catalytic applications.

Two Pd(0)–DIOP complexes (**Scheme 2**), $Pd(diop)_2$ (**1**)[2]–[4] and $Pd(\eta^2\text{-}CH_2{=}{=}CH_2)(diop)$ (**2**),[5] which were catalysts of asymmetric hydrocyanation of olefins, were reported

so far and their solution behavior was investigated by NMR. Both complexes were prepared by reduction of $PdCl_2$(diop) in the presence of DIOP or ethylene, respectively. The low-temperature ^{31}P NMR spectra of complex **1** show a pair of triplets, indicating that there are two pairs of magnetically inequivalent phosphorus nuclei in the complex. This observation is consistent with the tetrahedral geometry of Pd(0).



Phenyl groups are omitted for clarity.

Scheme 2

X-ray single crystal structure study of the complex **2** revealed that the C—C bond of the ethylene ligand in **2** (1.366 Å) was much shorter than those in analogous ethylene complexes of Ni(0) and Pt(0).[5] The shortness of the ethylene carbon–carbon bond in **2** accords with the relatively poor π-donor ability of the d^{10} palladium species. The weaker π-donation from the palladium center in **2** results in the weaker Pd–ethylene bond. Indeed, exchange between the coordinating and free ethylenes was observed by NMR. In the ^1H NMR spectrum of **2**, signals due to the pairs of diastereotopic coordinated ethylene proton are detected in the absence of free ethylene.

The Pd((*R*)-binap)$_2$ species, which was an active catalyst for asymmetric Heck reaction, was prepared. However, little is known about its characterization. Only the ^1H and ^{31}P NMR data were reported, which showed nothing significant.[5]–[7]

D. DIVALENT CHIRAL PALLADIUM COMPLEXES

The majority of chiral palladium complexes belong to the class of divalent chiral palladium complexes. Because of a large number of reported chiral Pd(II) species, they will be grouped in the following three categories. The first category is cyclometallated chiral Pd(II) complexes. Although applications of these palladacycles in organic synthesis are limited, they are still a very important class of compounds in coordination chemistry and

will be discussed independently. The second group is the chiral Pd(II) complexes without π-allyl ligands. The third group is chiral Pd(II) complexes with π-allyl ligands. The reaction patterns of π-allylpalladium complexes are different from those of palladium species without π-allyl moieties. Accordingly, they will be treated in separate sections.

D.i. Cyclometallated Chiral Pd(II) Complexes

Cyclopalladated complexes, which are most commonly prepared from tetrachloropalladate(II) and appropriate amines or imines, have drawn the attention of inorganic, coordination, and organometallic chemists[8] since the first report in 1965 (for imines) and in 1968 (for amines) by Cope and co-workers.[9],[10] These palladacycle species can easily be transformed into chiral form by employing corresponding chiral amines or imines. Two representative examples of the chiral cyclopalladated species are illustrated in **Figure 1**. This section will describe three examples that represent applications of these chiral orthometallated palladium complexes in organic synthesis.

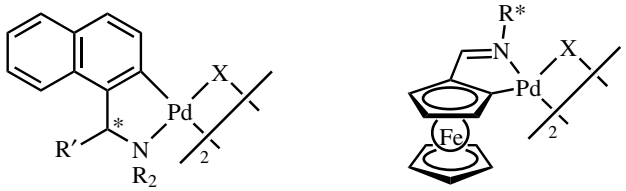
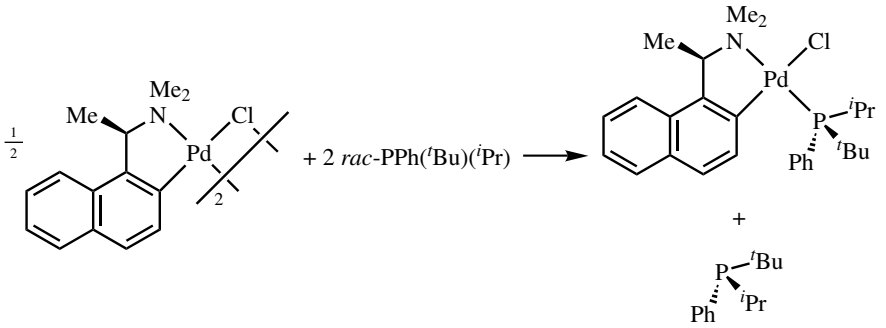


Figure 1

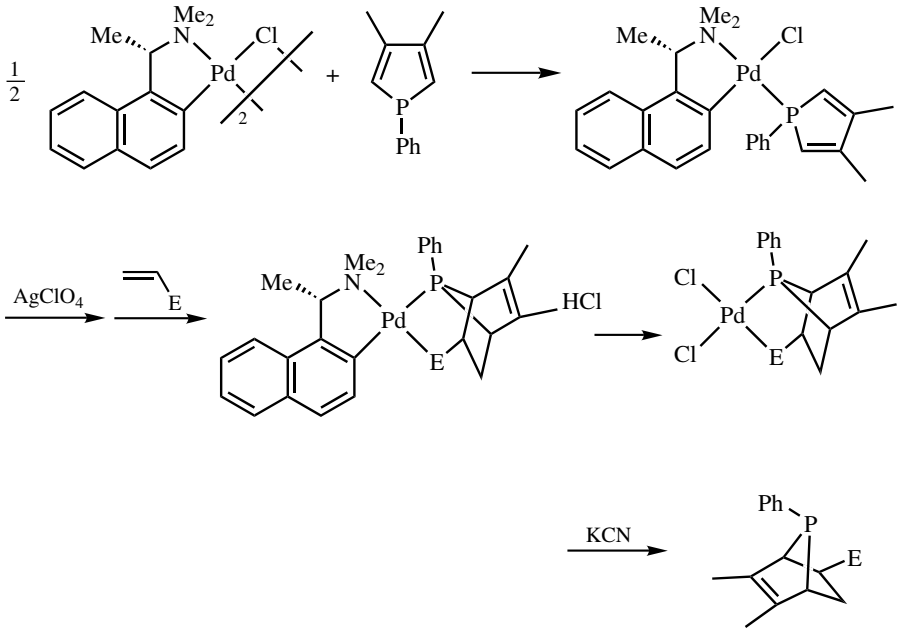
In 1971, an interesting application of the chlorobridged Pd(II) complexes with orthometallated chiral amines was demonstrated by Otsuka and co-workers: resolution of racemic chiral phosphines.[11],[12] The binuclear species reacts with tertiary phosphines or arsines to form two equivalents of mononuclear complexes (**Scheme 3**). If both the phosphines and the orthometallated palladium complexes were chiral, the mononuclear products could be a mixture of diastereomers. With appropriate combinations of the chiral racemic phosphines and the enantiomerically pure orthometallated palladium species, one of the two enantiomers of the phosphines reacts with the palladium complex selectively to give a specific diastereomer of the mononuclear palladium complexes, leaving the other enantiomer of the phosphine unreacted.



Scheme 3

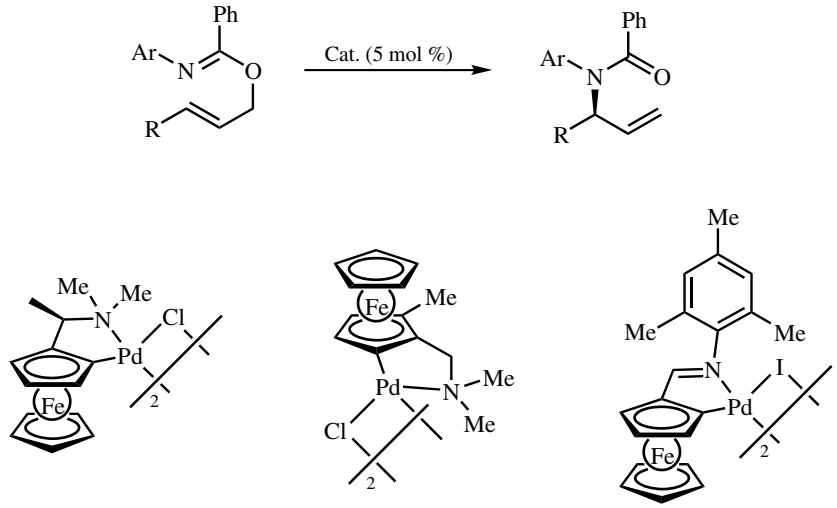
This method was applied to resolution of some important chiral phosphine ligands, which included the original resolution method of racemic BINAP.[13] The methodology of resolutions of tertiary phosphines and arsines has recently been reviewed.[14]

An interesting application of the chiral cyclopalladated complexes is palladium-promoted asymmetric Diels–Alder reactions of 1-phenyl-3,4-dimethylphosphole (**Scheme 4**). In the original report on the Diels–Alder reaction of the phosphole reported by Nelson and co-workers, the dichloropalladium species was employed as a promoter.[15] In 1994, Leung showed that a chiral cyclopalladated complex was capable of promoting the Diels–Alder reaction. In this reaction, the chiral palladacycle worked as a chiral auxiliary and showed almost perfect diastereoselectivity.[16] It has been revealed that simultaneous precoordination of a diene and a dienophile to the palladium center is essential for the reaction. Thus, both dienes and dienophiles should possess Lewis basic functionality. The diene 1-phenyl-3,4-dimethylphosphole has been the only substrate examined so far, while a variety of dienophiles, such as vinylphosphine,[16]–[21] vinylsulfoxide,[22] vinylsulfide,[23] acrylamide,[24] vinylarsine,[25] vinylpyridine,[26] vinylpyrrole,[27] or methylenequinuclidinone,[28] have successfully been applied to this asymmetric Diels–Alder reaction.



Scheme 4

The first examples of the use of cyclopalladated complexes in enantioselective catalysis were reported in 1997 by Overman et al.[29],[30] They applied a series of chiral cyclopalladated complexes to the rearrangement reactions shown in Scheme 5 and found that the palladium catalysts with ferrocene planar chirality exhibited good catalytic activity and enantioselectivity.



Scheme 5

D.ii. Palladium(II) Complexes with Chiral Phosphorus, Nitrogen, or Sulfur Ligands

D.ii.a. ***Dihalopalladium(II) Complexes.*** One of the first applications of chiral Pd(II) species to organic synthesis was asymmetric Grignard cross-coupling. The most common precursors to the catalysts are in the form of $PdCl_2$(L—L), where L—L is a chiral ligand. It was found that the chiral ligands having both phosphorus and nitrogen donors showed excellent enantioselectivity in Pd-catalyzed Grignard and organozinc cross-coupling. The first generation of these chiral ligands are chiral ferrocenyl phosphines reported by Hayashi et al.[31],[32] The dichloropalladium complexes of (*S*)-(*R*)-ppfa (**3**) and (*S*)-(*R*)-bppfa (**4**) (**Figure 2**) have different coordination mode: P, N-chelation for **3** and P, P for **4**. The difference of coordination fashion was reflected in their ^{1}H NMR characteristics. The two methyl groups of NMe_2 moiety in **3**, which coordinates to the Pd, are now diastereotopic and give two singlet resonances in the ^{1}H NMR spectrum. On the other hand, the NMe_2 in **4** gives a singlet because of fast inversion at the "free" nitrogen center.[31] In a series of dichloropalladium complexes of C_2 symmetric ferrocenyl-aminophosphine (**5**), the ferrocenyl ligands act as bisphosphine ligands and the nitrogen atoms are not bound to the palladium.[33]–[35] Several palladium complexes with ppfa analogs (**6, 7**) were prepared and applied to asymmetric Grignard cross-coupling.[36],[37] In all cases, the coordination spheres around the palladium centers are very similar and no distinctive distortion from square planar are seen.

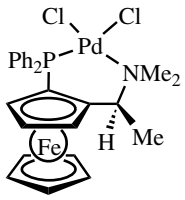
Aminophosphine ligands, which are derivatives of amino acids, also bind to $PdCl_2$ fragments in the bidentate way with the phosphorus and the nitrogen atoms.[38],[39] ^{1}H NMR spectra of **8**–**12** (**Figure 3**) supported coordination of the amino groups. The singlet NMe_2 resonances in the free ligands were shifted downfield in the complexes and appeared as pairs of two diastereotopic singlets. The fact excluded coordination of the sulfide groups in **11** and **12**.[39] Similar coordination was also observed in the phosphinopyrrolidine complex **13**.[40]

Generally, PdX_2L_n complexes are thermally stable, tolerant to air, and easy to handle. In addition, the dihalopalladium complexes frequently show good crystallinity. For

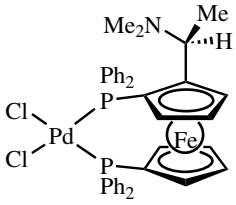
TABLE 1. Chiral Pd(II) Complexes without π-Allyl Ligands.

Complex	Precursor	Chirality[a]	Donor	Reaction[b]	X-ray[c]	NMR[d]	Ref.
3	$PdCl_2(MeCN)_2$	c; C, pl; ferrocene	N, P	Grignard cc[e]	n	H	31
4	$PdCl_2(MeCN)_2$	c; C, pl; ferrocene	P, P	Grignard cc[e]	y	H	31, 32
5	$PdCl_2(MeCN)_2$	c; C, pl; ferrocene	P, P	Grignard cc[e]	y	H	33, 34, 35
6	$PdCl_2(MeCN)_2$	c; C, pl; ferrocene	N, P	Grignard cc[e]	y	n	36
7	$PdCl_2(PhCN)_2$	c; C, pl; ferrocene	N, S	Grignard cc[e]	y	H	37
8, 9, 10	$PdCl_2(MeCN)_2$	c; C	N, P	Grignard cc[e]	n	H	38
11, 12	$PdCl_2(PhCN)_2$	c; C	N, P	Grignard cc[e]	y	H	39
13	Na_2PdCl_4	c; C	N, P	Grignard cc[e]	y	H, C, P	40
14	$PdCl_2(MeCN)_2$	c; S (sulfoxide)	S, S	allylation	y	n	41
15	$PdCl_2(MeCN)_2$	c; C, pl; ruthenocene	P, P	silylation	y	H, P	42
16	$PdCl_2(PhCN)_2$	c; C	P, P	allylation	y	H, C, P	43
17	$PdCl_2(MeCN)_2$	c; S (sulfoxide)	P, S	allylation	y	n	44
18	$PdCl_2$(cod)	c; C	P, S		y	H, C, P	45
19	$PdCl_2(PhCN)_2$	c; C (menthyl), P	P	hydrosilylation	n	H, C	46, 47
20	$PdCl_2(MeCN)_2$	ax; binaphthyl	P	hydrosilylation	y	n	48
21	$PdBr_2$	c; C, pl; ferrocene	P, P		y	H, C, P	49, 50
22	$PdCl_2(MeCN)_2$	ax; binaphthyl (binap)	P, P	silylation	y	n	7, 53
23	$PdCl_2$(cod)	c; C, pl; ferrocene	N, P	hydrosilylation	n	H, C, P	54
24	$Pd(OCOCF_3)_2$	c; C (oxazoline) ax; binaphthyl	N, N	Wacker	y	H, C	55
25	$Pd(OCOCF_3)_2$	ax; binaphthyl	N, N	Wacker	y	H, C	56
26	$Pd(OAc)_2$	c; C (oxazoline)	N, N	Fijiwara–Moritani	y	n	57
27	$PdCl_2$(PP)	ax, biphenyl	P, P	Heck	y	H, C, P	58
28	PdMeCl(cod)	c; C (oxazoline)	N, N	cyclization/H-Si	n	n	59
29	$PdCl_2(PhCN)_2$	c; C	P, C, P	aldol	y	H, C, P	60
30	$[Pd(NCMe)_4](BF_4)_2$	c; C (oxazoline)	N, N, N	aldol	y	H, C	61
31	$PdCl_2(PhCN)_2$	c; C	N, N	rearrangement	y	H	62
32	$PdCl_2$(binap)	ax; binaphthyl (binap)	P, P	aldol	y	H	63
33	$PdCl_2$(binap)	ax; binaphthyl (binap)	P, P	Mannich	y	H	64
34	$PdCl_2(MeCN)_2$	c; C (oxazoline)	N, N, P, P	allylation	y	H, C, P	65
35	PdMeCl(cod)	c; C(oxazoline)	N, N	polymerization	n	n	66
36	$[Pd(NCMe)_4](BF_4)_2$	c, C(Duphos)	P, P	polymerization	n	P	67
37	PdMeCl(cod)	ax; binaphthyl	P, P	polymerization	y	H, P	68

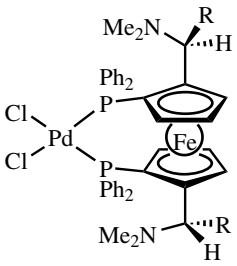
[a]Type of chirality: c = central chirality (with central atoms), pl = planar chirality, ax = axial chirality.
[b]Reactions to which the Pd complexes are applied as catalysts/reagents.
[c]y: with X-ray crystal structures, n: no crystal structure.
[d]Nuclei whose NMR data are reported.
[e]Grignard cc = Grignard cross-coupling.



$PdCl_2$((*S*)-(*R*)-ppfa) (**3**)



$PdCl_2$((*S*)-(*R*)-bppfa) (**4**)



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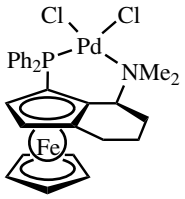

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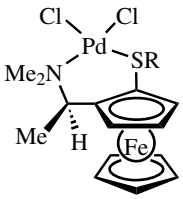

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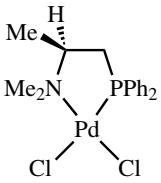
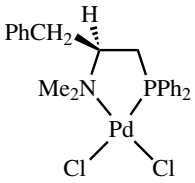
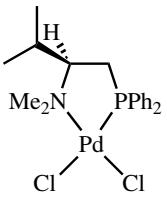
Figure 2



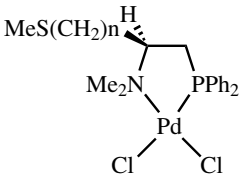
$PdCl_2$((*S*)-alaphos) (**8**)



$PdCl_2$((*S*)-phephos) (**9**)



$PdCl_2$((*S*)-valphos) (**10**)



11: $n = 2$; **12**: $n = 3$

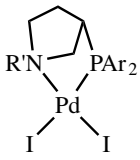


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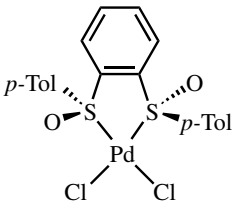
Figure 3

this reason, PdX_2 moieties are excellent templates for determining structures of chiral ligands by X-ray single crystal diffraction. Several chiral palladium complexes of this type were prepared and studied by X-ray crystallography, although the dihalopalladium complexes were not catalytically active species (or precursors) of reactions to which the chiral ligands were applied. These included the complexes listed in **Figure 4**. Two halide ligands tend to possess two adjacent coordination site of the square planar palladium (*cis* complexes; **14**–**18**)[41]–[45]; however, with certain steric bulkiness in the ligands, the complexes take a *trans* geometry (**19** and **20**).[46]–[48] Interesting examples are Pd–TRAP complexes **21**.[49],[50] The TRAP ligands are specially designed bidentate chiral phosphines whose bisferrocenylene backbones prevent them from coordinating in a *cis* fashion.



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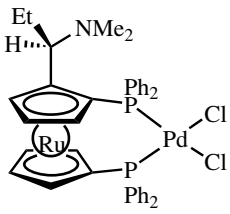

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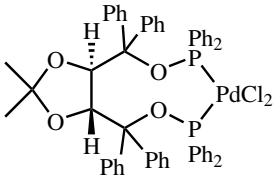

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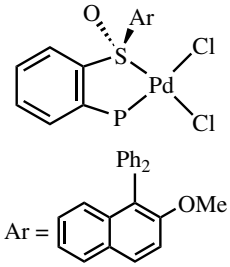

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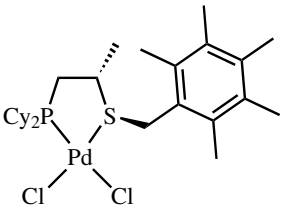

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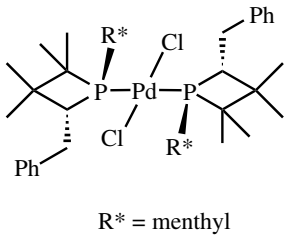

R* = menthyl

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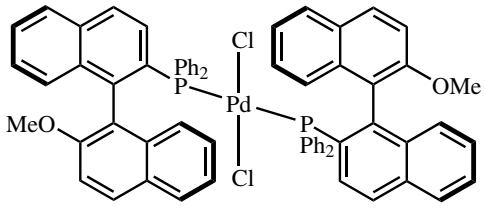

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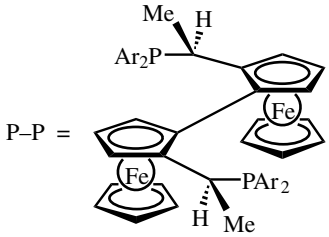
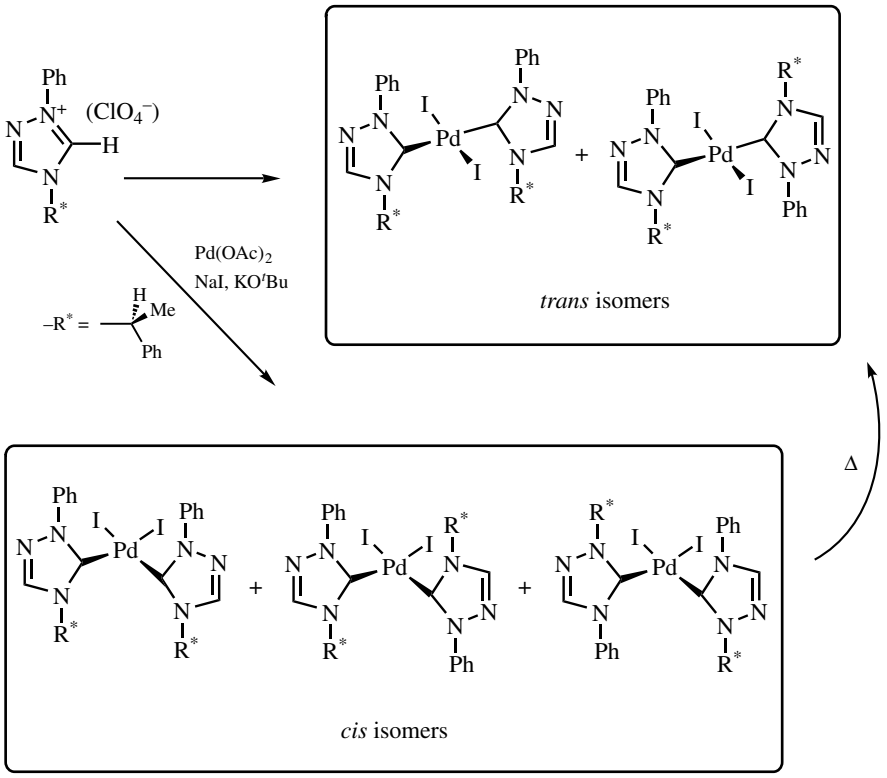


21: *trans*-$PdBr_2$(P—P)

Figure 4

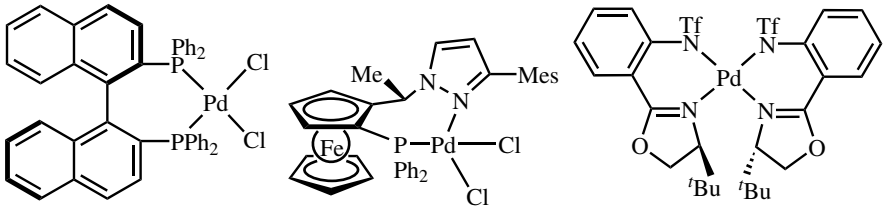
Chiral imidazolium or triazolium salt reacted with $Pd(OAc)_2$ in the presence of NaI and KO^{t}Bu, giving a mixture of carbene–Pd complexes (**Scheme 6**).[51] These nucleophilic carbenes are regarded as replacements of phosphines with stronger Lewis basicity and attracted considerable attention recently.[52] The palladium complexes formed as mixture of *cis* and *trans* isomers, which were separable by column chromatography. Upon heating in DMF at 100 °C, the *cis* isomer is completely isomerized into the *trans* isomer. In these complexes, rotations around the carbene–Pd bonds are restricted, probably due to double bond characters of the C—Pd bonds, and several diastereomers were detected.



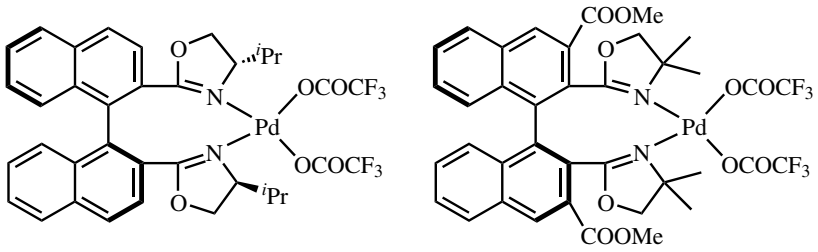
Scheme 6

Other miscellaneous examples of this series are listed in **Figure 5**.[7],[53],[54] Complex **22** showed large distortion from the normal square planar geometry, and the bite angle of the BINAP ligand (92.69°) was among the largest values for transition metal–BINAP complexes.[7]

Complexes **24**, **25**, and **26** all possess two neutral and two anionic ligands, respectively, and they are included in this section although they do not have halide ligands. Each of C_2-symmetric bisoxazoline complexes **24** and **25** has two trifluoroacetate ligands and is a good catalyst for asymmetric Wacker-type cyclization.[55],[56] Complex **26**, applied to the asymmetric Fujiwara–Moritani reaction, is a rare example of having anionic chelate



22 **23** **26**

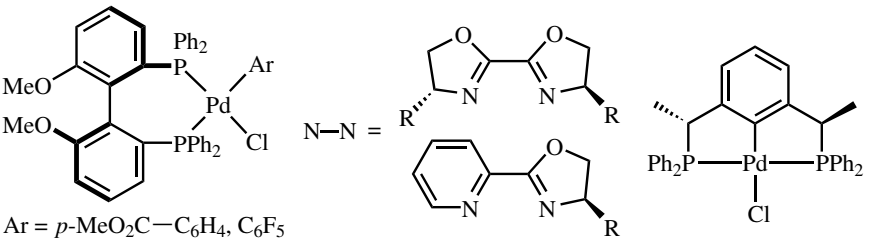


24 **25**

Figure 5

ligands.[57] The mechanistic study suggested that a species having only one ligand might be a real catalytically active species.

D.ii.b. ***Complexes with Carbon–Palladium σ-Bonds.*** Complexes having a hydrocarbyl ligand and a halide ligand are key intermediates of several Pd-catalyzed reactions (e.g., Heck reaction), although not many chiral species of this class are structurally characterized. Complex **27** (**Figure 6**) is one of the rare examples of these and represents a stabilized (by electronically with electron-withdrawing aryl group) intermediate of the asymmetric Heck reaction.[58] In **27**, the Pd—P bond *trans* to the aryl ligand is lengthened, indicating strong *trans* influence from the aryl ligand. The methyl–chloro complexes **28** were converted to cationic species *in situ* and employed to asymmetric cyclization/hydrosilylation.[59] Complex **29** has a unique chiral PCP tridentate ligand, which is prepared via cyclopalladation.[60] The complex is C_2-symmetric with two fused five-membered chelate rings. The two phenyl groups on the PPh_2 moieties are in pseudoaxial and pseudoequatorial positions, respectively. The arrangement of the phenyl



Ar = *p*-MeO_2C—C_6H_4, C_6F_5

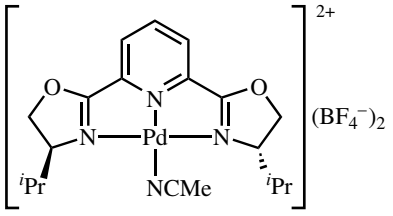
27 **28**: PdMeCl(N—N) **29**

Figure 6

groups is retained in the solution: the diastereotopic phenyls give two sets of resonances in the ^{1}H and ^{13}C NMR spectra.

D.ii.c. ***Cationic Pd(II) Complexes.*** The most preferred coordination number for Pd(II) complexes is four. When more than two neutral ligands coordinate to a divalent palladium, the complex becomes cationic. Anions such as halide can be potential ligands, which may replace the coordinating neutral ligands. To prevent the counteranions from coordination, weakly coordinating anions (noncoordinating anions) such as BF_4^- are frequently employed for these complexes.

The *cis*-N—Pd—N angles in **30** (**Figure 7**) are 79.5° and 81.8°, respectively, leaving a relatively large opening in the fourth coordination position for a potential reaction site upon dissociation of the acetonitrile.[61] X-ray crystallography of **31** reveals that the structure of the complex is C_1 symmetric because of the bend of the chloride bridges.[62] This bent structure is retained in solution: ^{1}H NMR gives two methyl signals with equal intensity. The aqua complex **32** and the hydroxo complex **33** were obtained from the same precursor $PdCl_2$(binap).[63],[64] Treatment of the dichlorocomplex with $AgBF_4$ in wet acetone gives **32**. Reaction with additional molecular sieves 4A leads to **33**. The counteranions in **34** are chlorides, which are potential ligands to the Pd.[65] The ionic form of **34** can be attributed to the chelate effect of the tetradentate ligand.



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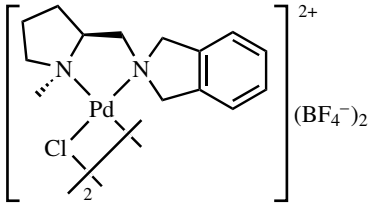

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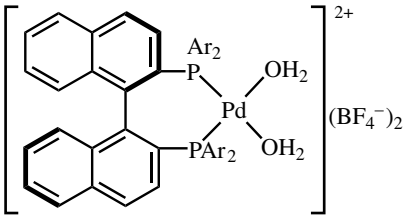

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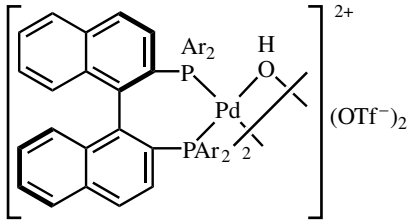

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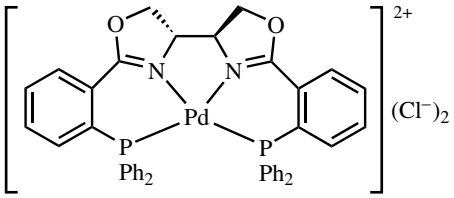

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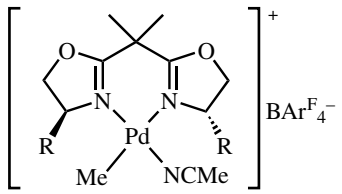
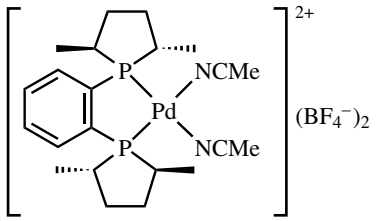
Figure 7



35: R = Me, ^{i}Pr



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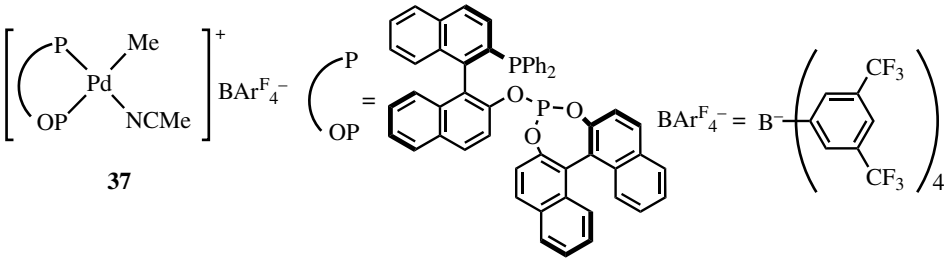

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Figure 8

An interesting application of cationic chiral Pd(II) complexes is copolymerization of olefin with carbon monoxide, which forms optically active, isotactic polyketones.[66]–[68] While complexes **35** and **36** (**Figure 8**) have C_2-symmetric chiral ligands,[66],[67] the chiral ligand in **37** is unsymmetric C_1 phosphine–phosphite with two independent binaphthyl skeletons.[68]

D.iii. Palladium Complexes with π-Allyl Ligands

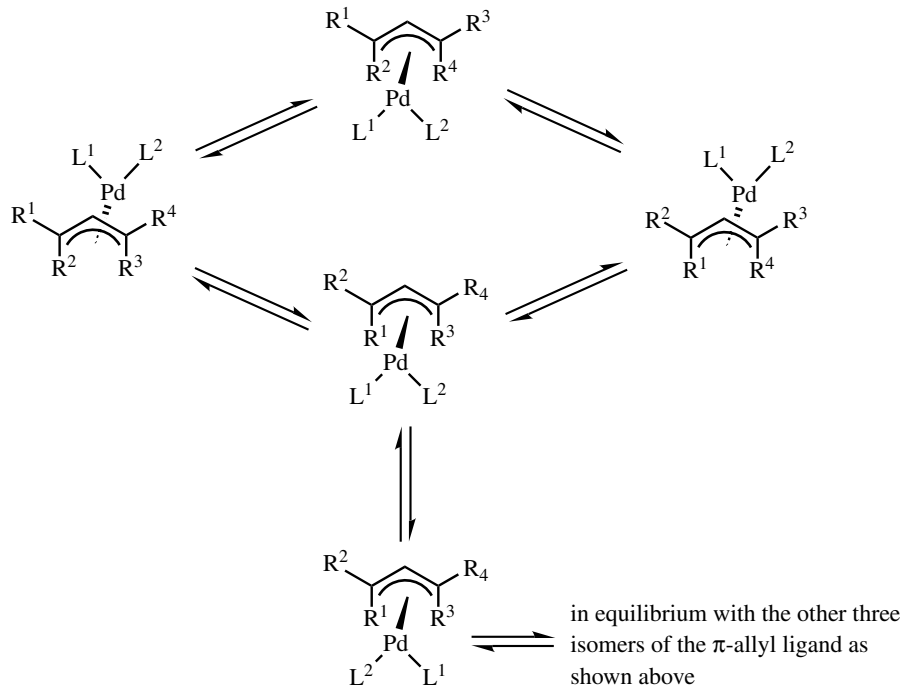
The π-allylpalladium species is a very important class of compounds in organopalladium chemistry, which can be a catalyst and/or a key intermediate of a variety of reactions, such as allylation of nucleophiles and reduction of allylic esters with formic acid. Most of these reactions are now developed to asymmetric reactions using appropriate chiral ligands. Usually, the π-allylpalladium complexes exist as rather complicated isomeric mixtures of stereoisomers as shown in **Scheme 7**, and controlling the equilibrium is one of the key factors to high stereoselectivity of the reaction. The isomerization of the π-allylpalladium complexes proceeds via a so-called π-σ-π process, and a total of eight isomers is possible for the very general example described in **Scheme 7**. However, most of π-allylpalladium systems studied in detail are not as complicated as **Scheme 7**. If the supporting ligands L^1 and L^2 are the same monodentate ligands or a C_2-symmetric bidentate ligand, the bottom half of **Scheme 7** can be negligible. Likewise, with certain substituted π-allyl ligands (e.g. $R^1 = R^2$), the isomerization becomes much simpler. In addition, in a system $L^1 \neq L^2$, steric and/or electronic effects from the supporting ligands may disallow existence of certain isomers.

D.iii.a. ***π-Allylpalladium Complexes with Chiral Monodentate Ligands.*** Several π-allylpalladium complexes with chiral monodentate phosphines are reported (**38**–**43**), **Scheme 8**.[69]–[74] In each complex, one equivalent of the phosphine ligand coordinates to

TABLE 2. Chiral Pd(II) Complexes with π-Allyl Ligands

Complex	Chirality[a]	Donor	Reaction[b]	X-ray[c]	NMR[d]	Ref.
38	ax; binaphthyl (MOP)	P	reduction w/ formic acid	y	H, P	69
39	ax; binaphthyl (MOP-phen)	P	reduction w/ formic acid	y	H, P	70
40	c; C (menthyl), P	P	allylation	y	H, C, P	71
41	c; C (menthyl), P	P	hydrovinylation	y		72
42	ax; binaphthyl	P	reduction w/ formic acid	y		73
43	c; P	P	hydrovinylation	y	H, P	74
44	c; C, pl; ferrocene	P, P	allylation	y	H, P	75
45	c; C	P, P	allylation	y	H, C, P	76
46	c; C (oxazoline)	N, P	allylation	y	H	77
47	c; C, pl; ferrocene	P, P	allylation	y	H, C, P, noesy	78
48	c; C pl; ferrocene/ruthenocene	P, P	allylation	y	H, C, P	79
49	c, pl; Fc-oxazoline	N, P	allylation	y	H, C, P, noesy	80
50	c; C	N, N	allylation	y	H	81
51	c; S (sulfoximine)	N, N	allylation	y	n	82
52	c; C	N, S	allylation	y	H	83
53	c; C (oxazoline)	N, P	allylation	y	H, P	84
54	pl; ferrocene, ax; binaphthyl	N, P	allylation	y		85
55	c; C (oxazoline), ax; binaphthyl	N, P	allylation	y	C, H, P	86
56	c; C	P, S	allylation	y		87
57	c; C (chiraphos)	P, P	allylation	y	H, C, P	88, 91
58	ax; binaphthyl (binap)	P, P	allylation	y	H, C, P	92, 93
59	c; C (chiral π-allyl)	η^3-C_3	allylation, Wacker	n	H	102, 103
60	c; C (chiral π-allyl)	η^3-C_3	Wacker	n	H	104
61	c; C (chiral π-allyl)	η^3-C_3	allylation	n	n	105
62	c; C (chiral π-allyl)	η^3-C_3		n	H, C	106
63	c; C (chiral π-allyl)	η^3-C_3		y	H, C	106
64	c; C (chiral π-allyl)	η^3-C_3		y	H, C	106

[a]Type of chirality: c = central chirality (with central atoms), pl = planar chirality, ax = axial chirality.
[b]Reactions to which the Pd complexes are applied as catalysts/reagents.
[c]y: with X-ray crystal structures, n: no crystal structure.
[d]Nuclei whose NMR data are reported.

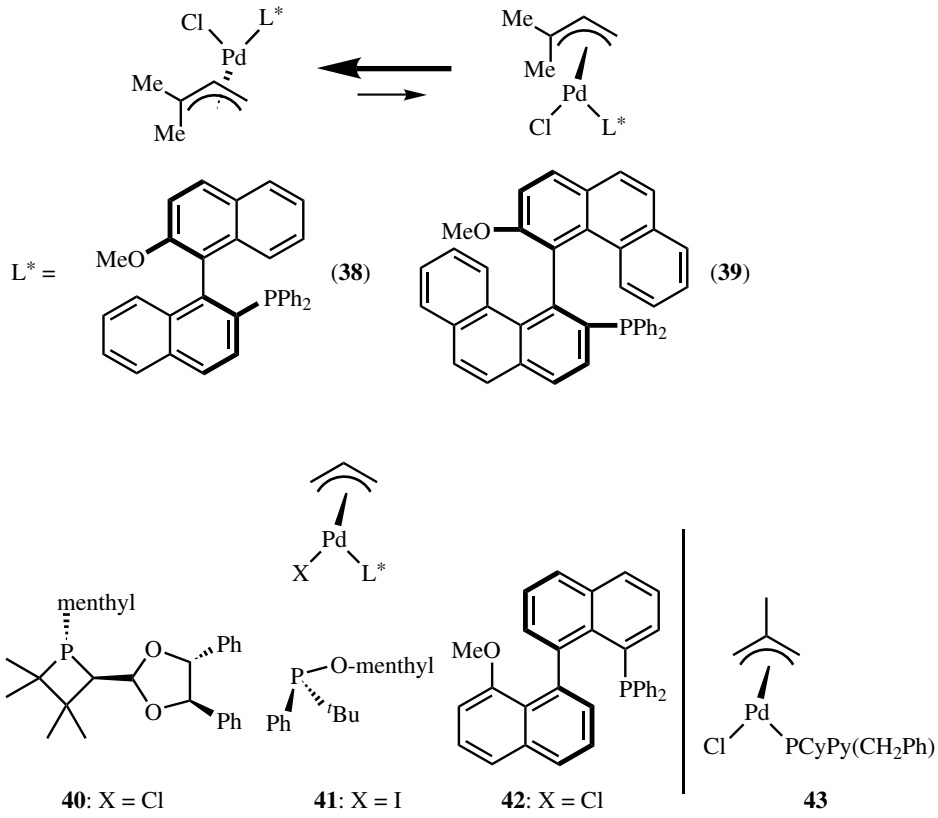


Scheme 7

the π-allylpalladium moiety and the last coordination site is filled by a halide ligand. Thus, all the complexes are obtained as neutral species. The solution NMR studies of **38** clarified that the π-allylpalladium complex existed as a mixture of the two diastereomers (**Scheme 8**).[69] The other possible isomers, in which the phosphine is *trans* to the CH_2 moiety of the π-allyl ligand, were not detected by NMR. Similar solution behavior was observed for **39** and **43** as well.[70],[74] Although analogous isomerization is assumed for all of the complexes in solution, the crystal structures of the complexes show the existence of only the major isomers in the solid state. Complexes **38**, **39**, and **42** were applied to asymmetric reduction of allylic esters with formic acid, in which use of monodentate chiral phosphine ligand was essential because of mechanistic requirement.[69],[70],[73]

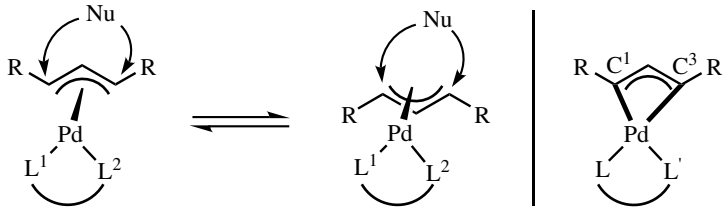
D.iii.b. ***π-Allylpalladium Complexes with Chiral Bidentate Ligands.*** The major part of the complexes in this category feature a distinctive steric characteristic: C_1-symmetric supporting chiral ligands. In fact, many of chiral C_1-symmetric bidentate ligands were designed and synthesized for the purpose of application to the π-allylpalladium catalysts.

The concept of C_2-symmetric ligands has widely been recognized as an ideal design of asymmetric ligands, which include DIOP, chiraphos, and BINAP. These ligands have been applied to a variety of transition metal-catalyzed asymmetric reactions and have been fairly successful. However, this situation is not always applied to π-allylpalladium-mediated asymmetric allylic substitutions. In the reaction, which has been the most frequently examined asymmetric reaction catalyzed by π-allylpalladium complexes, two factors need to be controlled for the sake of high stereoselectivity. One is



Scheme 8

the diastereomeric ratio between the two diastereomeric intermediates; the other is the position to which a nucleophile attacks (**Scheme 9**). The nucleophilic attack of soft nucleophiles comes from the opposite face of the π-allyl moiety with respect to the palladium center. Since the reaction sites are apart from the chiral ligands (L^1 and/or L^2), steric control of the two reaction sites by the coordinating chiral ligand is not always easy. A solution to this problem is C_1-symmetric bidentate ligand ($L^1 \neq L^2$). The difference of electronic properties between L^1 and L^2 is transmitted to the two possible reaction sites of the π-allyl ligand through the palladium center as a *trans* influence; then the electronic discrimination of the two reaction sites can be achieved.



Scheme 9

Some representative C_1-symmetric bidentate ligands, of which X-ray crystal structures of π-allylpalladium complexes are reported, are listed in **Figure 9**.[75]–[87] The magnitude of electronic discrimination between the two reaction sites in the π-allyl ligands can be estimated by the difference of the bond lengths between Pd-C^1 and Pd-C^3 of the symmetric π-allyl ligands (see **Scheme 9**). These values are 0.02 Å (**44**, R = H),[75] 0.10Å (**45**, R = Me),[76] 0.12 Å (**46**, R = H),[77] 0.07 Å (**47**, R = H),[78] 0.02 Å (**48**: M = Fe,

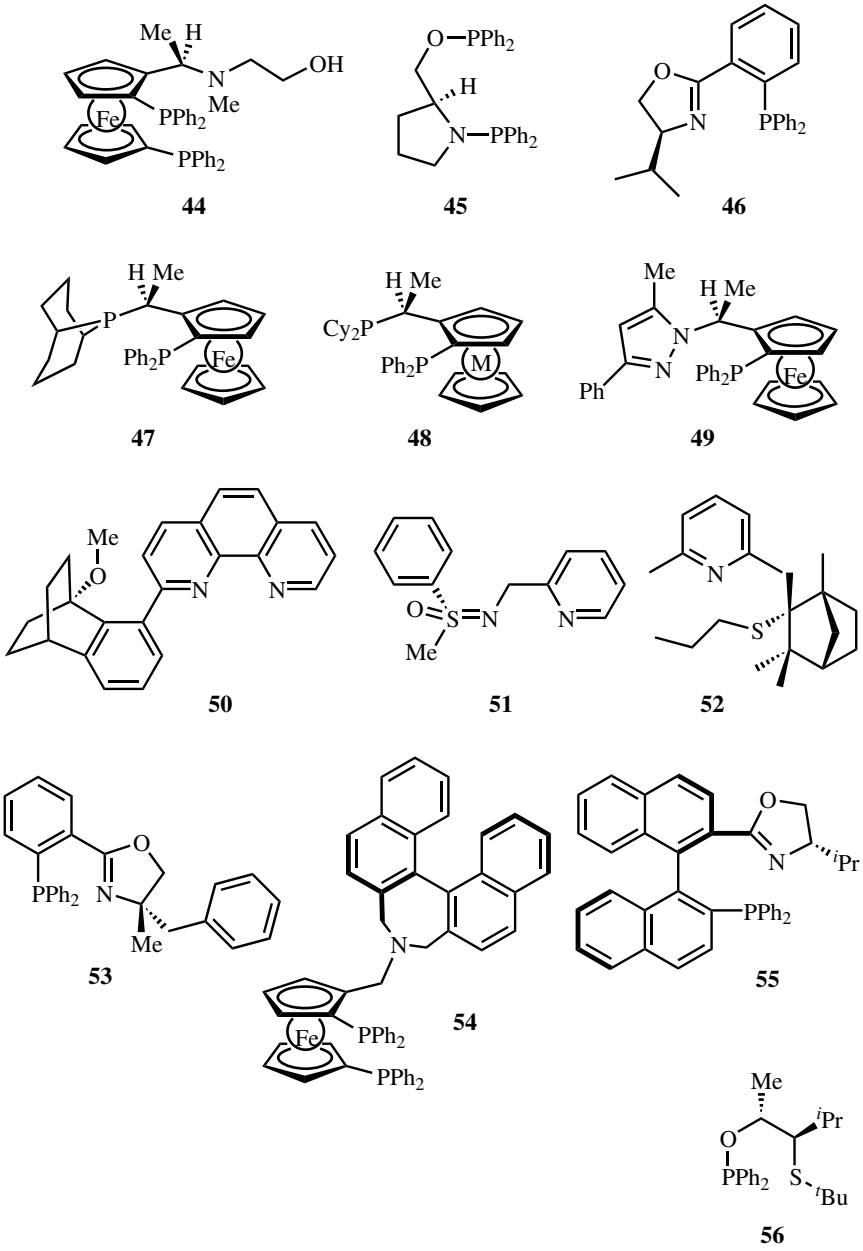
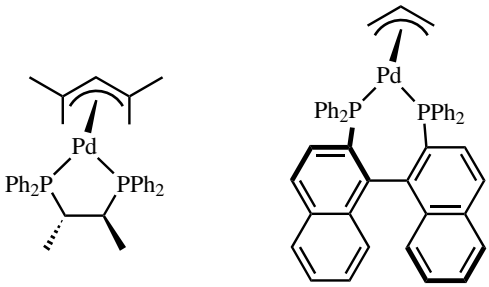


Figure 9

R = H),[79] 0.05 Å (**48**: M = Ru, R = H),[79] 0.13 Å (**49**, R = Ph),[80] 0.01 Å (**51**, R = H),[82] and 0.12 Å (**53**, R = H).[84]

Although examples are few, there still are some interesting examples of π-allylpalladium complexes with C_2-symmetric bidentate chiral ligands. The first thorough investigation on solution behavior of chiral π-allylpalladium complexes was done using the complexes of (*S*,*S*)-chiraphos, $Ph_2PC^*HMeC^*HMePPh_2$ (**57**, **Figure 10**).[88]–[90] The complexes were also employed as catalysts of asymmetric allylation. It was clarified that there was an approximate correlation of the enantioselectivity with the diastereomeric ratio of the corresponding π-allylpalladium intermediates.[88] The solid-state structure of the chiraphos complex was later reported independently.[91] Examples of BINAP-π-allylpalladium species are also known.[92],[93] The BINAP complex **58** was applied to catalytic asymmetric allylation using prochiral nucleophiles, α-acetamido-β-ketoesters, which gave chiral quaternary carbon centers with high enantioselectivity.[93]



57 **58**

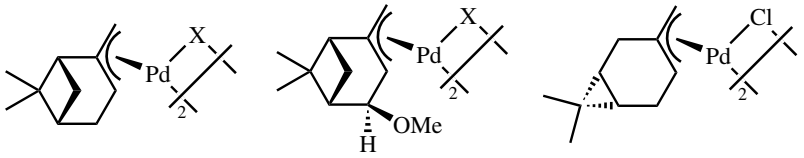
Figure 10

As shown in **Scheme 7**, the solution behavior of π-allylpalladium complexes is fairly complicated and analysis of the behavior is an interesting subject in conjunction with stereoselectivity of π-allylpalladium-catalyzed asymmetric reactions. These studies are beyond the scope of this review. If interested, see the references.[94]–[101]

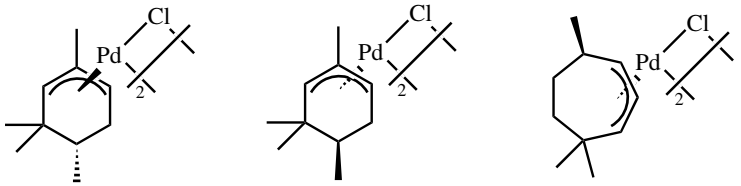
D.iii.c. ***Complexes with Chiral π-Allyl Ligands.*** Chirality can be introduced to the π-allyl moieties of the palladium complexes. Some representative examples are shown in **Figure 11**. The chiral sources of these π-allyl species are chiral terpenes. The terpenes (−)-β-pinene, pinadiene (for **60**), and (+)-3-carene (for **61**) reacted with $Pd(OAc)_2$ to give **59**,[102],[103] **60**,[104] and **61**,[105] respectively. Meanwhile, these terpenes reacted with the palladium-hydride species generated *in situ*, giving ring opening products **62**–**64** in high yield.[106] These complexes were applied to Wacker-type oxidation[103],[104] or allylation of imines.[105]

D.iv. Miscellaneous Chiral Pd(II) Complexes

Unique helical chirality was induced in the backbone of poly[2,3-(1,4-diazanaphthalene)], which was prepared by Pd-catalyzed polymerization of 1,2-diisocyanobenzenes.[107] The catalyst precursor was **65**, which showed no helical chirality, and reacted 5

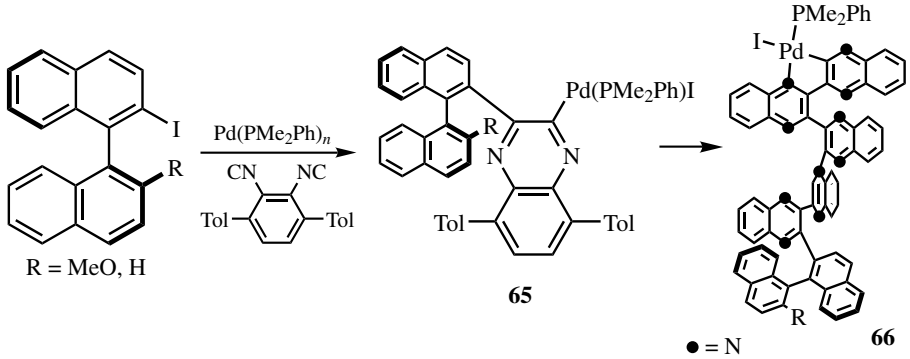


59: X = Cl, OAc **60**: X = Cl, OAc **61**



62 **63** **64**

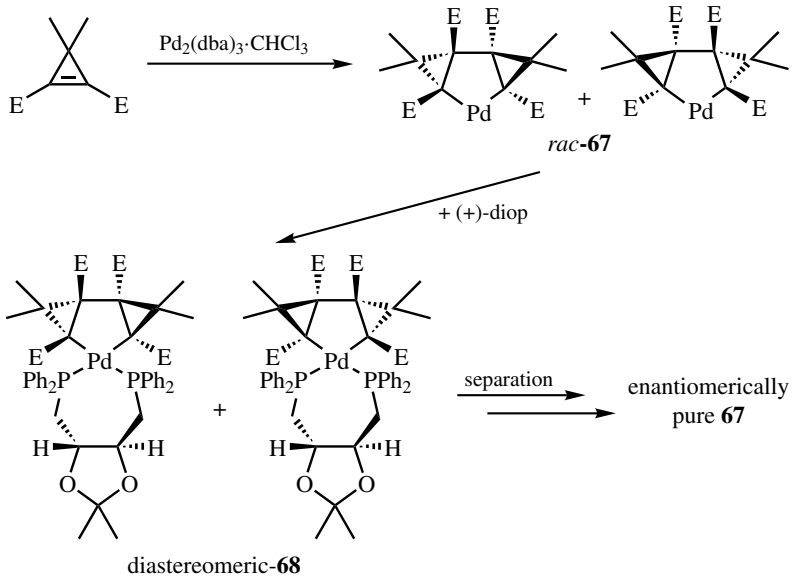
Figure 11



Scheme 10s

equiv of the monomer to give a diastereomeric mixture of pentamer–Pd complexes **66**. The diastereomers could be separated and the diastereomerically pure complex **66**, which was still an active polymerization catalyst, gave the enantiomerically pure helical polymer (**Scheme 10**).

The 1,2-bis(methoxycarbonyl)-3,3-dimethylcyclopropene reacted with $Pd_2(dba)_3 \cdot CHCl_3$ in acetone to give an enantiomeric mixture of the helically chiral palladacycle complex **67**, which was solvated by acetone. The palladacycle reacted with (+)-DIOP to give a diastereomeric mixture of **68**. The diastereomers were easily separated by HPLC, and removal of the DIOP ligand afforded the enantiomerically pure palladacycle (**Scheme 11**).[108] Using chiral C_2-symmetric cyclopropenes (with chiral ester groups) in place of the achiral cyclopropene as a starting compound gave analogous chiral palladacycles with high diastereoselectivity.[109]



Scheme 11

E. SUMMARY

Although the coordination chemistry of Pd(0) and Pd(II) is not so attractive from the inorganic chemist's point of view, a fairly large number of chiral species have been reported. Since this section has excluded the chiral palladium complexes generated *in situ*, a number of chiral palladium species actually utilized in organic synthesis should be much bigger. A lot of interest in chiral palladium complexes can be attributed to their synthetic usefulness in organic chemistry. Considering the central roles of asymmetric synthesis and transition metal-catalyzed reactions in modern synthetic chemistry, many more chiral palladium complexes will be added to the list in the near future.

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