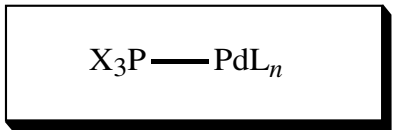


II.2.3 Pd(0) and Pd(II) Complexes Containing Phosphorus and Other Group 15 Atom Ligands

DANIÈLE CHOUEIRY and EI-ICHI NEGISHI

A. TYPES OF PALLADIUM–PHOSPHORUS COMPLEXES AND SOME REPRESENTATIVE PALLADIUM–PHOSPHORUS COMPLEXES OF SYNTHETIC SIGNIFICANCE

The Pd – P bonded complexes may contain phosphines (i.e., PR_3), phosphites [i.e., $P(OR)_3$], and/or other trivalent phosphorus compounds with C, H, N, and other heteroatom substituents. However, by far the most important Pd–P complexes from organic synthetic viewpoints are those containing triorganylphosphines, and they will mainly be considered in this section. Those Pd–P complexes that contain chiral ligands are discussed later in **Sect. II.7**. Phosphorus compounds may be mono-, bi-, and multidentate compounds containing one or more phosphorus atoms. Both monodentate and bidentate phosphines and some related phosphites have been shown to be synthetically important, but the use of tridentate and more highly multidentate phosphorus compounds is still very rare. Some representative Pd–phosphine complexes containing monodentate and bidentate phosphines of synthetic significance are listed in **Tables 1** and **2**, respectively. Some other achiral phosphines and phosphites that have been incorporated mainly *in situ* into Pd complexes are listed in **Table 3**.

B. PREPARATION AND *IN SITU* GENERATION OF PALLADIUM–PHOSPHORUS COMPLEXES

The majority of the Pd–P complexes listed in **Tables 1** and **2** are commercially available. For various reasons, however, it may be useful to prepare them or know how they are prepared. For example, $Pd(PPh_3)_4$ is relatively unstable to oxygen. So, in some cases, one may prefer preparing and using it before its degradation. In general, Pd–P compounds may be either prepared as isolable and storable compound or generated *in situ* in the reaction system.

Although metallic palladium is the source of Pd for essentially all Pd compounds, Pd(II) salts containing halogens and/or oxygen ligands, such as $PdCl_2$, M_2PdCl_4

Handbook of Organopalladium Chemistry for Organic Synthesis, Edited by Ei-ichi Negishi
ISBN 0-471-31506-0

TABLE 1. Some Synthetically Significant and Well-Characterized Palladium–Phosphine Complexes Containing Achiral Monodentate Phosphines

Carbon Number	Pd–Phosphine Complex	Commercial Availability	References for Preparation
12	$Cl_2Pd(PEt_3)_2$	+	[1]
16	$Cl_2Pd(PPhMe_2)_2$	+	[2]
24	$I_2Pd[P(Bu\text{-}n)_3]_2$	−	[3]
	$Cl_2Pd(TFP)_2$[a]	−	[4]
26	$Cl_2Pd(PPh_2Me)_2$	+	[5]
36	$Pd(PCy_3)_2$	+	[6]
	$Cl_2Pd(PPh_3)_2$	+	[7]
	$Br_2Pd(PPh_3)_2$	+	[8]
	$I_2Pd(PPh_3)_2$	−	[8]
	$Cl_2Pd(PCy_3)_2$	+	[9]
40	$(AcO)_2Pd(PPh_3)_2$	+	[10]
42	$Cl_2Pd(TTP)_2$[a]	+	[11]
52	$Pd(PPh_2Me)_4$	+	[6]
72	$Pd(PPh_3)_4$	+	[12]

[a] TFP = Tris(2-furyl)phosphine. TTP = Tris(*o*-tolyl)phosphine

(M = Li, Na, K), and $Pd(OAc)_2$, generally serve as immediate precursors to Pd–P complexes (**Protocol 1**, **Scheme 1**). In some cases, these halogen- and oxygen-containing Pd complexes are converted first to Pd complexes containing carbon and other types of ligands, such as $Pd(dba)_2$ and $Cl_2Pd(PhCN)_2$, which may then be converted to Pd–P complexes (**Protocol 2**, **Scheme 1**). It should also be noted that even some phosphorus-containing

TABLE 2. Some Synthetically Significant and Well-Characterized Palladium–Phosphine Complexes Containing Achiral Bidentate Phosphines

Cabon Number	Pd–Phosphine Complex	Commercial Availability	References for Preparation
26	$Cl_2Pd(Ph_2PCH_2CH_2PPh_2)$[a]	+	[13]
	$Br_2Pd(Ph_2PCH_2CH_2PPh_2)$[b]	−	[14]
27	$Cl_2Pd[Ph_2P(CH_2)_3PPh_2]$[c]	−	[15]
28	$Cl_2Pd[Ph_2P(CH_2)_4PPh_2]$[d]	−	[16]
34	$Cl_2Pd(Ph_2PCpFeCpPPh_2)$[e]	+	[17]
42	$Cl_2Pd(Ph_2PC_{20}H_{14}PPh_2)$[f]	−	[18]
52	$Pd(Ph_2PCH_2CH_2PPh_2)_2$[g]	+	[19]

[a] $Cl_2Pd(dppe)$.

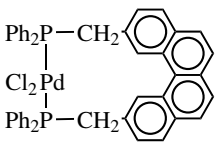
[b] $Br_2Pd(dppe)$.

[c] $Cl_2Pd(dppp)$.

[d] $Cl_2Pd(dppb)$.

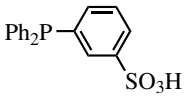
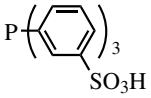
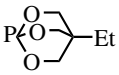
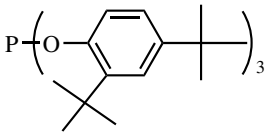
[e] $Cl_2Pd(dppf)$.

[f] Transphos =



[g] $Pd(dppe)_2$.

TABLE 3. Some Achiral Phosphines and Phosphites Incorporated in Synthetically Useful Palladium–Phosphorus Complexes

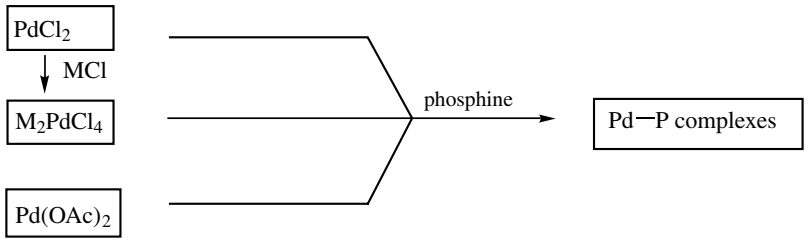
Carbon Number	Pd–P Complex	Acronym or Abbreviation	Commercial Availability	References for Preparation
Phosphines				
15	$(i\text{-Pr})_2P(CH_2)_3P(Pr\text{-}i)_2$	dippp	−	[20]
16	$(i\text{-Pr})_2P(CH_2)_4P(Pr\text{-}i)_2$	dippb	−	[21]
17	$Ph_2PCH_2CH_2NMe_3X$		−	[22]
18		DPMSPP	+	[23]
		TMSPP	+	[24]
Phosphites				
3	$P(OMe)_3$		+	[25]
6	$P(OEt)_3$		+	[26]
		TMPP	−	[27]
9	$P(OPr\text{-}i)_3$		+	[28]
18	$P(OPh)_3$		+	[29]
42			+	[30]

complexes [e.g., $Cl_2Pd(PPh_3)_2$ and $Pd(PPh_3)_4$] as well as various organopalladium complexes [e.g., $PhCH_2Pd(PPh_3)_2Cl$] can serve as precursors to Pd–P complexes.

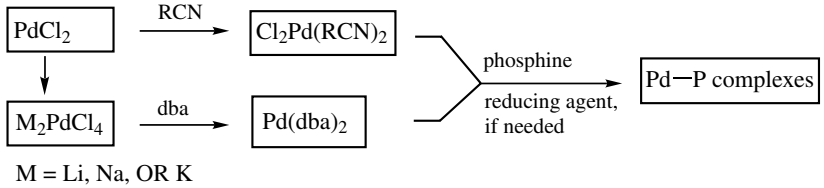
More specifically, Pd(II)–phosphine complexes of the $Cl_2Pd(II)(PR_3)_2$ type, such as $Cl_2Pd(II)(PPh_3)_2$,[7] and even those containing bidentate ligands, such as $Cl_2Pd(II)(dppp)$,[15] can be most conveniently prepared from $M_2Pd(II)Cl_4$ and $Cl_2Pd(II)(PhCN)_2$ according to the general equations shown in **Scheme 2**. The direct use of $PdCl_2$ can be complicated by its low solubility in most organic solvents, while M_2PdCl_4 and $Cl_2Pd(PhCN)_2$ are soluble in various organic solvents, such as THF and MeOH. The preparation of Pd(0)–phosphine complexes of the $Pd(0)(PR_3)_4$ type, such as $Pd(0)(PPh_3)_4$,[31] and the related complexes containing bidentate phosphines, such as $Pd(dppe)_2$,[32],[33] can be most conveniently achieved using $Pd(0)(dba)_2$ and related Pd(0)–dba complexes.[34] Alternatively, Pd(II) complexes, such as $PdCl_2$ and M_2PdCl_4, may be used as Pd sources in conjunction with external reducing agents, such as hydrazine hydrite[12] and *n*-BuLi,[35] as indicated by several methods for the preparation of $Pd(PPh_3)_4$ shown in **Scheme 3**, which are readily adaptable to the synthesis of others represented by $Pd(0)(PR_3)_4$.

Many different kinds of reducing agents can be used for reducing Pd(II) compounds to Pd(0) compounds. It is, however, advisable to choose reagents that do not produce undesirable by-products. The use of external reducing agents is desirable in cases where Pd–P

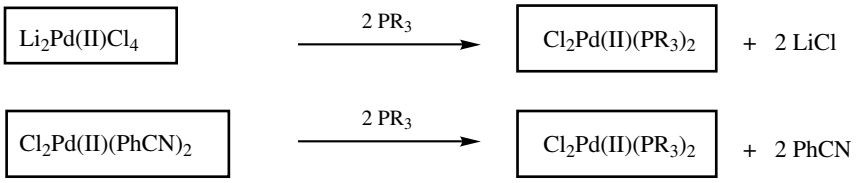
Protocol 1



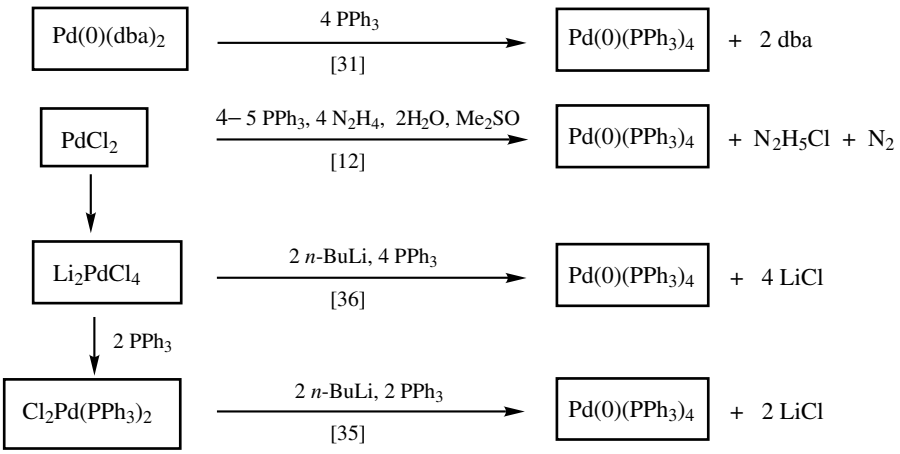
Protocol 2



Scheme 1



Scheme 2



Scheme 3

complexes are to be prepared and isolated. On the other hand, in cases where Pd–P complexes are to be generated *in situ* as catalysts, external reagents are often unnecessary, since a wide variety of organic compounds including olefins, alcohols, amines, phosphines, organometals, metal hydrides, and CO are capable of the required reduction. Some representative examples of such reduction reactions are shown in **Scheme 4**, and they are further discussed in detail in later parts.

C. SELECTION OF STRUCTURAL PARAMETERS

Selection of a Pd–P complex as a catalyst for a given desired synthetic transformation may still be largely an empirical matter. Even so, it is useful to be familiar with some general trends and guidelines for finding optimal structural parameters, such as the oxidation state of Pd, types and structures of ligands, and electron counts.

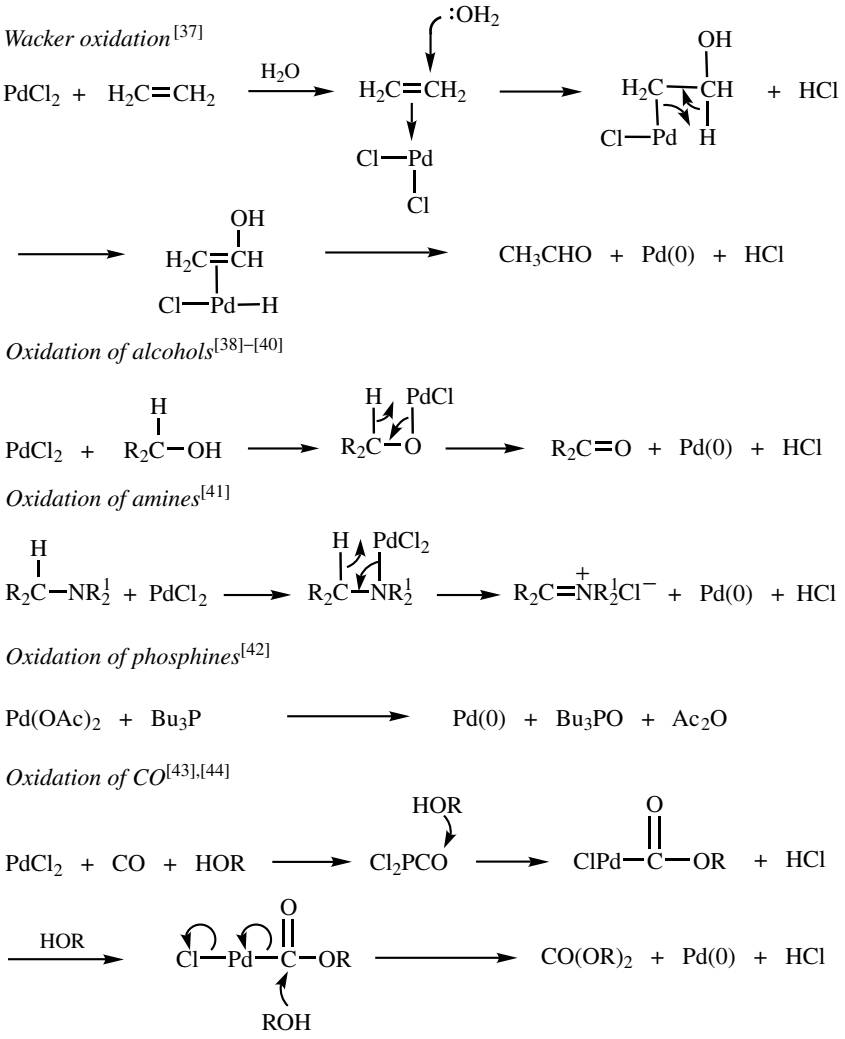
C.i. Pd(II) Versus Pd(0)

Some Pd-catalyzed reactions, such as cross-coupling and the Heck reaction, are thought to be initiated by Pd(0) complexes, while the others, such as the Wacker oxidation, are thought to be initiated by Pd(II) species. And yet, most of the Pd-catalyzed reactions involve at least a pair of redox processes. In such cases, the catalytic cycles involve both Pd(0) and Pd(II) species, and, in principle, catalysis may be initiated by either Pd(0) or Pd(II) complexes of appropriate structures. Coupled with the ease with which Pd(II) compounds are reduced to Pd(0), as shown in **Scheme 4**, selection of Pd catalysts of the appropriate oxidation state is in most cases a relatively insignificant matter. Thus, for example, both Pd-catalyzed cross-coupling and the Heck reaction have been performed with either Pd(0) or Pd(II) complexes. In cases where Pd(0) complexes are desired as initiating catalytic species, reduction of Pd(II) precatalysts is effected by one or more of the reactants, added ligands, and solvents, even though some such processes might be rather sluggish. Consequently, no external reducing agents may be needed. On the other hand, in cases where the desired catalytic cycle is to be initiated by Pd(II) complexes, as in the Wacker oxidation, Pd(0) complexes generated as products of the desired transformation or added as precatalysts must usually be oxidized back to Pd(II) species by external oxidants. Such processes are usually stoichiometric in oxidants. Selection of oxidants is discussed extensively in later parts (**Parts V**, **VI**, and **VIII**, in particular).

C.ii. Type and Structure of Phosphorus Ligands

Triphenylphosphine appears to be by far the least expensive phosphine at present. For a combination of reasons, it is also one of the most effective ligands. For example, the effects of phosphines on the ease of reductive elimination from $R^1_2Pd(PR_3)_2$ are summarized in **Table 4**.[45] The results indicate that the efficiency of phosphines decreases in this order: $PPh_3 > PPh_2Me > PPhMe_2 > PEt_3$. Although not fully clarified, the order may be inversely proportional to their basicity and/or proportional to their steric requirements. The comparative significance of basicity may be indicated by a higher level of efficiency observed with P(2-furyl)$_3$[46] in some cross-coupling reactions.[47]–[51] Probably for the same reason, trialkylphosphines are much less effective in Pd-catalyzed cross-coupling.

In general, Pd(0) complexes display their nucleophilic or basic properties more strongly than their electrophilic properties, whereas the opposite is generally true with



Scheme 4

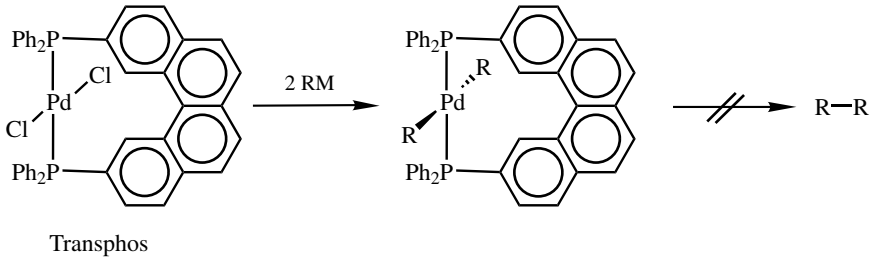
TABLE 4. Effects of Phosphines and Organolithiums on the Reductive Elimination Reaction of $R^1_2Pd(PR_3)_2$[45]

		Yield of R^1—R^1 from R^1Li (%)							
		PhLi		(*E*)-*t*-BuCH=CHLi		*t*-BuC≡CLi		MeLi	
$Cl_2Pd(PR_3)_2$	pK_a of RR_3	1h	3h	1h	3h	1h	3h	1h	3h
$Cl_2Pd(PEt_3)_2$	8.65	8	9	<2	<2	<2	<2	<2	<2
$Cl_2Pd(PPhMe_2)_2$	6.50	32	37	85	85	<5	<5	<5	<5
$Cl_2Pd(PPh_2Me)_2$	4.65	63	66	95	95	<5	<5	15	40
$Cl_2Pd(PPh_3)_2$	2.71	>95	>95	>95	>95	>95	>95	>95	>95

Pd(II) complexes. On this basis, any process involving Pd(0) complexes may be facilitated by highly basic phosphines and that involving Pd(II) complexes by phosphines of low basicity. However, most catalytic cycles involve both Pd(0) and Pd(II) complexes. So, the overall outcome depends on a combination of factors of which the rate-determining step and its location in the catalytic cycle must be most critical. For example, the relative rates of oxidative addition of aryl halides decrease in the order: ArI > ArBr > ArCl. In general, it has been difficult to use aryl chlorides in a synthetically useful manner, and the sluggish oxidative addition of aryl chlorides tends to make it the rate-determining step in most of their reactions. In such cases, strongly basic trialkylphosphines might be expected to be more effective than triarylphosphines. As a matter of fact, PCy_3[52],[53] and $P(t\text{-Bu})_3$[53] have been found to be very effective in promoting the Suzuki cross-coupling reaction of aryl chlorides and arylboronic acids. It is believed that both their electron richness and steric bulk are responsible for the observed reactivity. Similarly, their biphenyl analogs [i.e., 2-dicyclohexylphosphino and 2-di(*t*-butyl)phosphinobiphenyl] were found to lead to highly active catalysts for the room-temperature amination and Suzuki coupling of aryl chlorides.[54] Finally, recent papers report the successful use of $P(t\text{-Bu})_3$ for the Heck[55] and Stille[56] couplings of aryl chlorides.

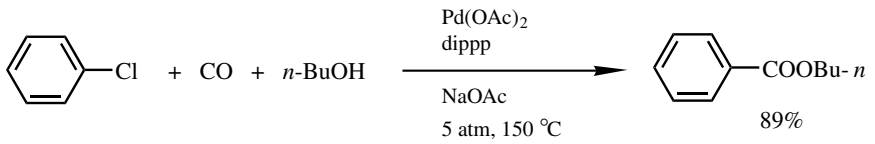
Bidentate phosphines have been shown to be very effective in many Pd-catalyzed reactions including cross-coupling. The most conspicuous feature of bidentate ligands is that they are restricted to occupy two coordination sites that are either *cis* or *trans* (in most cases *cis*) to each other. Another is greater thermal stability of Pd complexes containing then due to their bidentate nature. As reductive coupling of two ligands must require that they be *cis* to each other at the critical moment of coupling, the configurational rigidity that bidentate ligands impart to their Pd complexes has some profound effects on reductive elimination. In general, Pd-catalyzed reactions involving reductive eliminations, such as cross-coupling,[17],[57] are significantly facilitated by bidentate phosphines, such as dppp[17] and dppf.[17],[58] Some others, such as dppe[17] and dppb,[17] are generally less effective in Pd-catalyzed cross-coupling, suggesting that bite angle[57],[59],[59a] and some other intricate factors might be responsible for differentiating these structurally related phosphines. It was observed that both the selectivity and the rate of cross-coupling increase with increasing bite angle and reach an optimal value for dppf and DPEphos [2,2′-bis-(diphenylphosphino)diphenylether].[59] Larger bite angles result in a decreased selectivity and activity. Palladium complexes with dppf ligands were also found to greatly improve reactions such as the direct α-aryltion of ketones,[60] the amination of aryl halides,[61],[62] as well as the cross-coupling of arl chlorides with arylzincs.[63],[64] The rigid structure of Transphos[18] is such that the two P atoms can only be *trans* to each other. The two carbon groups in its square planar diorganyl derivatives must therefore be also *trans* to each other. Consequently, no reductive elimination has been observed with them[18] (**Scheme 5**). A recent paper reports, however, that in contrast to the stability of Pd(Transphos)$(R)_2$, the Pd(Transphos)(R)(SR) complexes undergo facile reductive elimination.[65] This unexpected observation is most likely the result of partial dissociation followed by reductive elimination from a three-coordinate species or isomerization to the *cis* complex, which is then expected in view of its large bite angle to undergo fast reductive elimination. Another potentially significant bidentate phosphine is dippp,[20] which has been shown to be effective in converting chlorobenzene to benzoic acid derivatives via carbonylation (**Scheme 6**).

Another important development is the preparation and use of water-soluble phosphines, such as TMSPP,[24] DPMSPP,[23] and $Ph_2PCH_2CH_2NMe_3X$ (X = halogen).[22] These water-soluble phosphines not only facilitate the separation of these ligands and



Transphos

Scheme 5



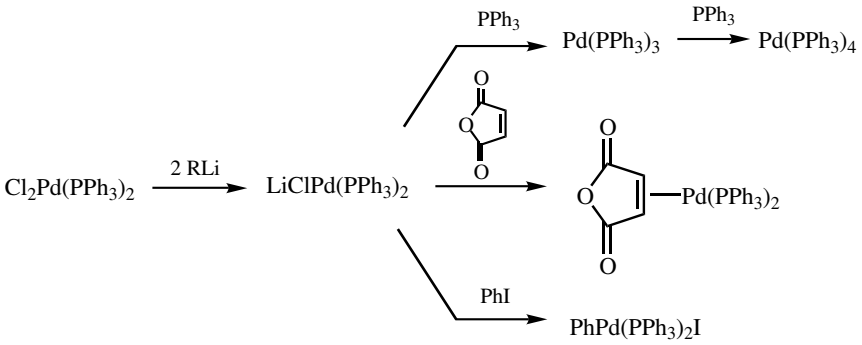
Scheme 6

their Pd complexes from organic products but also permit the use of Pd–phosphine catalysts under aqueous conditions.

Phosphites have not thus far been used as frequently as phosphines. Their generally lower σ basicity and higher π acidity reltive to phosphines are expected to find some synthetically useful applications. In this respect, a recent paper[30] reporting the use of various phosphites, in particular $[2,4\text{-}(t\text{-Bu})_2C_6H_3O]_3P$, in the Heck rection of aryl bromides and even some aryl chlorides is noteworthy. The use of a mixture of phosphines and phosphites, especially in the form of bidentate ligands containing both classes of P groups, is yet another largely unexplored possibility.

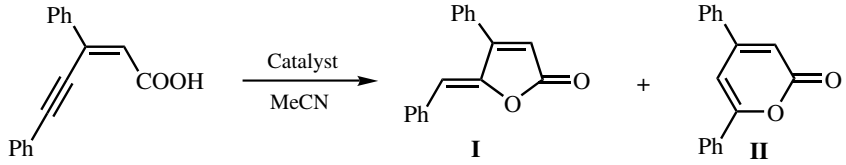
C.iii. Electron Count

In most cases, Pd–P complexes added to the reaction system serve as precatalysts, which must be first converted to active catalysts. For example, oxidative addition of iodobenzene with $Pd(PPh_3)_4$ to give $PhPd(PPh_3)_2I$ must first convert coordinatively saturated 18-electron $Pd(PPh_3)_4$ into coordinatively unsaturated Pd species. It is known to dissociate in solution into 16-electron $Pd(PPh_3)_3$ and even 14-electron $Pd(PPh_3)_2$. A recent study claims 12-electron $Pd(PPh_3)$ as an active species in oxidative addition.[66],[67] And yet, establishment of 14- and 12-electron species as active catalysts have been difficult. Despite the fact that some 14-electron $Pd(PR_3)_2$ containing very bulky phosphines have been prepared and identified as such,[68] there does not appear to be any report on the detection and characterization of genuine 14-electron $Pd(PPh_3)_2$. One attempt at its generation has led to the generation of 16-electron $LiClPd(PPh_3)_2$ and 18-electron $Li_2Cl_2Pd(PPh_3)_2$[35] (**Scheme 7**). A later detailed study has demonstrated the involvement of 16-electron $ClPd(PPh_3)_2^-$ and 18-electron $Cl_2Pd(PPh_3)_2^{2-}$ as active species in oxidative addition.[69] In view of the 18- and 16-electron rule,[70] it is reasonable to expect the difficulties encountered in detecting and characterizing genuine 14- and 12-electron species with ordinary ligands. This does not, however, rule out the involvement of such low electron count species as transient species in catalytic cycles. While this issue will continue to be controversial, what is synthetically important is the recognition that certain Pd complexes effectively act as low electron count species. Thus, in the oxidative addition of iodobenzene with $Pd(PPh_3)_4$, the Pd complex effectively



Scheme 7

acts as 14-electron $Pd(PPh_3)_2$ irrespective of the precise mechanism. Thus, two of the four PPh_3 ligands must be displaced. Furthermore, Pd–phosphine species in many Pd-catalyzed reactions appear to remain as Pd–bisphosphine complexes. In this sense, only two molecules of PPh_3 in $Pd(PPh_3)_4$ appear to be required in such reactions, and the other two may be unnecessary. This has indeed been the case in some Pd-catalyzed cross-coupling, as discussed in **Part III**. On the other hand, in some other reactions, $Pd(PPh_3)_4$ has been shown to be superior to $Pd(PPh_3)_2$ derivatives, as exemplified by the results shown in **Scheme 8**.[71]



Catalyst	**I** (%)	**II** (%)
$Cl_2Pd(PhCN)_2$	50	44
$Cl_2Pd(PPh_3)_2$	27	10
$Pd(PPh_3)_4$	83	6

Scheme 8

C.iv. Other Parameters

There can be various other synthetically important variations of Pd–P complexes. One is the use of chiral phosphines (**Sect. II.7**). Another is that of immobilized Pd–P complexes including polymer-bound Pd–P complexes (**Sect. II.8**). These topics are discussed in later sections indicated in parentheses.

D. PALLADIUM COMPLEXES CONTAINING NITROGEN AND ARSENIC LIGANDS

Although phosphines and phosphites are by far the most commonly used ligands for palladium, nitrogen- or arsenic-containing compounds having different electronic properties

can also serve as ligands, which can in many instances be significantly superior to the phosphorus-containing ligands.

D.i. Pd – N Complexes

Palladium will form complexes with the great majority of organic compounds containing nitrogen donor atoms. Some representative Pd–N complexes containing mono- and bidentate nitrogen ligands are summarized in **Table 5**.

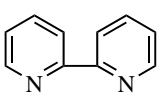
Among these complexes, $Cl_2Pd(MeCN)_2$ and $Cl_2Pd(PhCN)_2$ are probably the most useful from a synthetic point of view due to their high solubility in organic solvents and the ease of displacement of the RCN (R = Me, Ph) ligands, which often makes them the starting point of the generation of other Pd complexes (*vide supra*). These two complexes are commercially available but can be simply prepared by heating $PdCl_2$ in the corresponding nitrile. Another important monodentate complex is $(BF_4)_2Pd(MeCN)_4$, which serves as a catalyst for olefin isomerization and polymerization.[81]

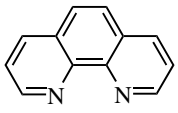
All of the complexes of **Table 5** are Pd(II) complexes. Pd(0) complexes, such as Pd(0)(Ph-BIAN), can be isolated as their dimethylfumarate or fumaronitrile complexes.[82]

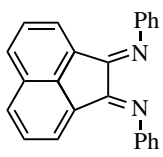
TABLE 5. Some Synthetically Significant and Well-Characterized Palladium–Nitrogen Complexes Containing Achiral Monodentate and Bidentate Nitrogen Ligands

Carbon Number Preparation	Pd–N Complex	Commercial Availability	References for
MONODENTATE			
0	$Cl_2Pd(NH_3)_2$	+	[72]
4	$Cl_2Pd(MeCN)_2$	+	[73]
8	$(BF_4)_2Pd(MeCN)_4$	+	[74]
14	$Cl_2Pd(PhCN)_2$	+	[75]
	$Br_2Pd(PhCN)_2$	+	[76]
16	$(OAc)_2Pd(NEt_3)_2$	−	[10]
BIDENTATE			
2	$Cl_2Pd(H_2NCH_2CH_2NH_2)$[a]	+	[77]
6	$Cl_2Pd(Me_2NCH_2CH_2NMe_2)$[b]	+	[78]
10	$Cl_2Pd(NC_{10}H_8N)$[c]	+	[79]
12	$Cl_2Pd(NC_{12}H_8N)$[d]	+	[79]
24	$Cl_2Pd(PhNC_{12}H_6NPh)$[e]	−	[80]

[a] $Cl_2Pd(en)$.
[b] $Cl_2Pd(tmeda)$.
[c] $Cl_2Pd(bipy)$.
[d] $Cl_2Pd(phen)$.
[e] $Cl_2Pd(Ph\text{-}BIAN)$.

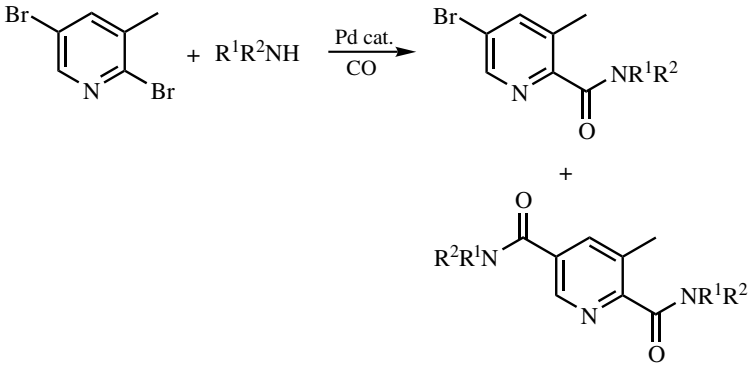
bipy = 

phen = 

Ph-BIAN = 

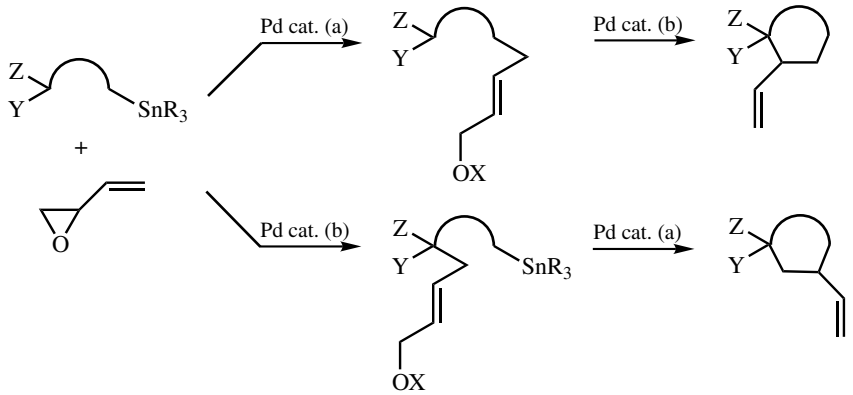
Pd–N complexes are usually prepared similarly to Pd–P complexes from $PdCl_2$, M_2PdCl_4 (M = Li, Na, K), $Cl_2Pd(PhCN)_2$, $Pd(OAc)_2$, or $Pd(dba)_2$. They can also be conveniently generated *in situ* from $Pd(OAc)_2$[83] or $Pd(dba)_2$[84],[85] and the corresponding ligand.

Although Pd–N complexes sometimes have catalytic activities that are comparable to that of the Pd–P complexes,[86],[87] they often lead to significantly different reactivity profiles as exemplified by the Pd-catalyzed regioselective carbonylation[83] (**Scheme 9**) or the selective activation of a switchable bisnucleophile[88] (**Scheme 10**). Other examples can be found in the catalytic hydrogenation of alkenes,[89] or the carbacyclization of enynes,[90] as well as in cross-coupling[80],[91],[92] and allylic substitution reactions.[93]



Entry	R^1R^2NH	Catalyst	Mono:Bis	Isolated Yield
1	$PhNH_2$	$Cl_2Pd(PPh_3)_2$	75:25	55%
2	4-$ClPhNH_2$	$Cl_2Pd(PPh_3)_2$	75:25	40%
3	$PhNH_2$	$Pd(OAc)_2$/bipy	98:2	82%
4	4-$ClPhNH_2$	$Pd(OAc)_2$/bipy	98:2	72%

Scheme 9



Pd cat. (a) = $Cl_2Pd(MeCN)_2$; Cl_2Pd(bipy)
Pd cat. (b) = $Pd(PPh_3)_4$

Scheme 10

Tridentate nitrogen ligands have also been used, and an exceptional η^1-allyl palladium complex containing terpy (2,2′:6′,2″-terpyridine) has been obtained as a result of the strong tendency of terpy to maintain tridentate coordination.[94]

Although no attempt has been made to systematize the role of N-ligands as has been done for P-ligands, their effects are both electronic and steric in nature. For instance, rate acceleration has been observed with the good donor ligands (e.g., bipy and Ar-BIAN) in some processes where oxidative addition appears to be the rate-determining step.[80] Especially interesting is the rigidity of the phen and Ar-BIAN ligands, which impedes partial dissociation and forces *cis* chelation particularly favorable to reductive elimination. Moreover, with bipy, phen, and Ar-BIAN, the steric bulk around the Pd reactive center can easily be modified by the addition of substituents.

Although still sporadic, it appears from the recent literature that the use of N-ligands is becoming more and more frequent and is very likely to be greatly expanding in the future.

The use of mixed phosphorus/nitrogen (P/N thereafter) bidendate ligands is another possibility that has already proved to be of great synthetic significance. Recent reports illustrate the use of an iminophosphine ligand in the Stille cross-coupling of aryl iodides with alkynyltributyltin compounds,[95] and in the Pd-catalyzed carbostannylation of alkynes.[96] In both cases, the Pd(0)-iminophosphine catalyst was superior to the corresponding phosphine complexes and a novel mechanism of action involving an oxidative addition into the C–Sn bond has been implicated.[97] On the other hand, an aminophosphine ligand was found to lead to a very highly reactive catalyst for the Suzuki coupling reaction and for the amination of unactivated aryl chlorides.[98] Finally, 2-pyridyldiphenylphosphines[99] and 2-pyrimidylphosphines[100] are excellent ligands for the Pd-catalyzed carbonylation of alkynes. In this case, X-ray analyses have identified cationic four-membered chelates intermediates based on P/N complexation, $(BF_4)_2Pd(P/N)_2$, which are relevant in the catalytic cycle.[100]

D.ii. As Ligands

Pd–As complexes have been known for several decades. **Table 6** lists some Pd–arsine complexes of both mono- and bidentate arsines.

$Pd(AsPh_3)_4$ was actually described in 1957,[101] but the first report on the use of a Pd–As complex was with $Cl_2Pd(AsPh_3)_4$ that was found to enhance the rate of carbonylation

TABLE 6. Some Synthetically Significant and Well-Characterized Palladium Complexes of Achiral Monodentate and Bidentate Arsine Ligands

Cabon Number	Pd–As Complex	Commercial Availability	References for Preparation
MONODENTATE			
6	$Cl_2Pd(AsMe_3)_2$	–	[1]
36	$Cl_2Pd(AsPh_3)_2$	–	[7]
40	$(AcO)_2Pd(AsPh_3)_2$	–	[10]
72	$Pd(AsPh_3)_4$	–	[101]
BIDENTATE			
26	$Cl_2Pd(Ph_2AsCH_2CH_2AsPh_2)$	–	[14]
30	$Cl_2Pd[o\text{-}C_6H_4(AsPH_2)_2]$	–	[102]

reactions.[103] Later, the use of $(AcO)_2Pd(AsPh_3)_2$ in cycloisomerization reactions was reported.[104]

It is, however, only in 1991 that Farina and Krishnan demonstrated in a very interesting and extensive study the superiority of the arsine ligands over the corresponding phosphine ligands in the Stille cross-coupling reaction of olefinic[48] stannanes with various electrophiles, for which rate accelerations as large as 10^3 were observed in some cases. Beyond the obvious synthetic interest, this finding shed some light on the mechanism of the Stille cross-coupling of olefinic stannanes. Indeed, a kinetic study provided evidence that the rate-determining transmetallation step[105] proceeds via ligand dissociation and formation of Pd–stannane double bond π-complex. The soft $AsPh_3$ ligand is both thermodynamically and kineticlly more labile than PPh_3 and thus facilitates the formation of such an intermediate. It is worth noting that, unlike PPh_3, the excess of $AsPh_3$ ligands was found to have essentially no inhibitory effect on the coupling rate, compensating the fact that a Pd:L stoichiometry of 1:4 seems necessary for optimum yields in the case of this less stable catalyst.[48]

The rate-accelerating effect of $AsPh_3$ was also observed in the coupling of arylstannanes with vinyl and aryl triflates, solving the reportedly difficult vinyl–aryl and aryl–aryl couplings.[106],[107] In this case, however, the similar ligand effect observed with tetrabutyltin suggests that no prior complexation with the stannane is necessary to justify the results.[107] A recent mechanistic study on the Stille coupling between perhalophenyl iodide and vinyl- or 4-anisyltributyltin ($RSnBu_3$) using $AsPh_3$ as a ligand (L) strongly questions a mechanism initiated by a dissociation of L and provides instead evidence for an associative L-for-R transmetallation step leading to a T-shaped three-coordinate *cis*-(PdR^1R^2L) from which irreversible reductive elimination must be fast.[108]

Regardless of the mechanistic interpretation, the $Pd/AsPh_3$ system has recently been extensively used. This has had a great impact on the development of the Stille reaction and other Pd-catalyzed processes. Indeed, this catalytic system has in many instances been found to give superior results to the corresponding phosphine analog. Moreover, it has made possible some reactions for which phosphine ligands have failed to work.[109]

No arsine ligands besides $AsPh_3$ have so far been investigated. The $Pd–AsPh_3$ complex is usually generated *in situ* from commercially available $AsPh_3$ in conjunction with a variety of Pd(0) or Pd(II) sources such as $Pd(dba)_2$,[110],[111] $Pd_2(dba)_3$,[112],[113] Pd/C,[114] $Pd(OAc)_2$,[114] $PdCl_2$,[115] or $Cl_2Pd(PhCN)_2$.[115]

E. SUMMARY: A PROTOCOL FOR THE SELECTION OF Pd COMPLEXES AND LIGANDS

E.i. Why Homogeneous Pd Complexes?

Metallic Pd and many of the Pd salts are polymeric and are often not readily soluble in organic and inorganic solvents with some notable exceptions, such as Li_2PdCl_4, which is readily soluble in THF and other organic solvents. Phosphorus and other neutral ligands containing groups 14–16 elements have been used to generate monomeric and oligomeric Pd complexes that can readily be dissolved in various solvents. Of these, those that contain P, especially phosphines, have been by far the most widely observed and used.

Aside from the solubility issue mentioned above, the relative order of "intrinsic" reactivity of Pd-containing species may be generalized as follows: monoatomic Pd vapor and cationic (and possibly anionic) Pd ions > coordinatively unsaturated

monomeric and oligomeric homogeneous Pd complexes > polymeric Pd metal and related species. However, monomeric (or even oligomeric) Pd vapor is a short-lived species that are readily converted to much less reactive polymeric Pd metal. Its life may be prolonged in the form of a cation (or perhaps an anion). Such metal cations have indeed been generated and shown to be of extremely high "intrinsic" reactivity. Their generation and reactions have thus far been observed only in mass spectrometers.

Polymeric Pd is a rather inert and hence precious metal that can be and has been activated and used in a limited number of reactions, such as hydrogenation and oxidation, often under rather forcing conditions. Conversion of polymeric Pd metal into homogeneous complexes usually *via* inorganic Pd salts (**Subsect. B**) then represents a reasonable compromise leading to the generation of soluble Pd species of varying degrees of reactivity.

E.ii. Selection of Homogeneous Pd Complexes.

This has been one of the most crucial and yet often difficult tasks in more demanding cases of the Pd-catalyzed organic synthesis. One of the relatively easy aspects is the choice of the starting Pd compounds. In most cases, Pd(II) compounds, such as (a) $PdCl_2$ and related halides, (b) $Pd(OAc)_2$, (c) M_2PdCl_4 (M = Li, Na, and K), and (d) some neutral ligand-containing derivatives of (a)–(c), such as $PdCl_2(RCN)_2$, as well as Pd(0) compounds, most notably $Pd(dba)_2$, $Pd(dba)_3$, and their other congeners have been used often interchangeably as precursors to those Pd complexes containing the desired ligands, as discussed in **Subsect. B**.

Also relatively straightforward is the choice between Pd(II) and Pd(0) complexes. Very few, if any, Pd-catalyzed reactions are catalyzed exclusively by Pd(0) complexes throughout an entire catalytic cycle. There are a limited but increasing number of reactions that must be exclusively catalyzed by Pd(II) complexes, where reduction of Pd(II) complexes to Pd(0) species is detrimental and is to be avoided.[116]] In such cases, Pd(II) rather than Pd(0) must obviously be chosen.

In most cases, however, the catalytic cycles must involve both Pd(II) and Pd(0) species, although even Pd(IV) species may also be involved in some cases (**Sect. II.4**). As long as both Pd(II) and Pd(0) species are involved in a catalytic cycle, appropriately ligated Pd complexes can enter the catalytic cycle as either Pd(II) or Pd(0) species. As discussed in **Subsect. B**, a wide variety of reagents present in the reaction mixtures including reactants, auxiliary reagents, such as amines, alcohols, carbon monoxide, and solvents have been shown to reduce Pd(II) compounds. Although generally less facile and hence more limited, Pd(0)-to-Pd(II) oxidation can also be achieved by various reagents present in the reaction mixtures. In some cases, however, deliberate reduction or oxidation by some external reagents added specifically for this purpose has been desirable or even required as in the Wacker oxidation.

E.iii. Selection of Ligands.

The most crucial and perhaps most difficult aspect in the selection of homogeneous Pd complexes is that of choosing the optimal ligand. This is also a rapidly evolving topic of the organopalladium chemistry. In most of the demanding cases, it is not easy to pick and specify the most optimal ligand for each case. It is nonetheless reasonable to initially consider phosphines and follow the selection protocol presented below.

Step 1: Using PPh_3, optimize both Pd complex structures and reaction conditions.

Unless known otherwise, PPh_3 may be chosen first, since it is one of the least expensive commercially available phosphines and since it has been shown to be generally effective and widely applicable. After all, roughly half, if not more, of the currently known Pd-catalyzed reactions of interest in organic synthesis appear to involve the use of PPh_3.

In cases where the reactants contain changeable parameters, such as (i) metal counter cations and (ii) halogen and other leaving groups, as in the Pd-catalyzed cross-coupling discussed in **Part III**, these parameters should be first optimized. There are usually only a few to ten or a dozen options with respect to these parameters, and only one to a few of them are worth serious considerations.

Next, the structure and method of generation of Pd-PPh_3 complex may be optimized by varying readily changeable parameters including (iii) PPh_3-to-Pd ratio and attendant electron count (**Subsect. C.iii**), (iv) Pd(II) vs. Pd(0) discussed above, (v) method of generations including the use of external reagents, such as *n*-BuLi and DIBAH (**Subsect. B**), (vi) solvents including generally favorable THF and DMF, (vii) added promoters and cocatalysts, such as $ZnCl_2$, $ZnBr_2$, LiCl, NaOH, NaOAc, K_3PO_4, Ag_2CO_3, H_2O, Et_3N, and other amines, and so on, and (viii) other reaction conditions including concentration, order of addition, temperature, pressure, and time.

Step 2: Find the optimal phosphine among those that are currently known.

In cases where the optimization of reaction parameters mentioned in *Step 1* using PPh_3 either is known not to give or does not actually give satisfactory results, the use of other phosphines may then be considered. Since many dozens of phosphines are currently known, the scope of this optimization process is significantly more extensive than that in *Step 1*. Moreover, it is still a largely empirical and time-consuming process. Even so, some useful generalizations and guidelines based on the currently available data may be exploited to facilitate the optimization process. Even in the absence of prior knowledge and experiences consultation with **Tables 1–3** (**Subsect. A**) may lead to reasonable lists of ten or so known phosphines each, such as that shown below.

It is useful to recall the following basic guidelines presented in **Sect. I.2** for further narrowing down the list of phosphines for optimization. First, Pd(0) complexes are generally more nucleophilic than electrophilic, while the opposite is generally true with Pd(II)

Monodentate Phosphines	Bidentate Phosphines
PPh_3 (Reference phosphine)	dppe
P(Bu-*t*)$_3$	dppp
PCy_3	dppb
P(Tol-*o*)$_3$ or TTP	dppf
TFP	dippp
	DPEphos

complexes. So, if either observed or anticipated difficulty is thought to lie in an oxidative step, namely Pd(0)-to-Pd(II) transformation, electron-rich phosphines, such as P(Bu-*t*)$_3$, PCy_3, and dippp, should be seriously considered. On the other hand, reductive processes may be promoted through the use of phosphines of lower basicity, such as TFP. In reality, however, most of the Pd-catalyzed processes involve both oxidative and reductive steps. It is therefore important to have some mechanistic insights and reasonable notions as to where the rate-determining step might be.

Second, various steric factors including *bite angles* are often critically important, but it appears unwise to try to dissect steric factors in one or even two dimensions, as they are undoubtedly multifaceted. For example, some sterically hindered phosphines including $P(Bu\text{-}t)_3$, PCy_3, $P(Tol\text{-}o)_3$, and dippp have been shown to be useful in various Pd-catalyzed reactions. It is conceivable that their ability to lead to the formation of Pd complexes of low electron count, such as 14- or even 12-electron species, by virtue of steric bulk might be significant. In such cases, steric and electronic factors are intricately intertwined and inseparable.

Third, bidendate phosphines have been shown to be very effective in an increasing number of Pd-catalyzed reactions, especially in those cases where β-H-containing alkylpalladium species are involved. It is indeed strongly recommended to consider their use in such cases. One of their distinguishing features is their ability to serve as chelating ligands. Here again, the effects of chelation are undoubtedly multifaceted. Chelation usually demands two coordination sites that are *cis* to each other. This, in turn, can enforce a *cis* relationship between two interacting ligands and promote their productive interaction. Here again, it appears that both steric and electronic factors including stereoelectronic effects are simultaneously involved, as discussed in **Subsect. C.ii**. Irrespective of mechanistic details, however, useful correlations between some structural parameters and desirable reaction characteristics have been experimentally observed. Bite angle [57][59][59a] appears to be a particularly useful parameter that can be either experimentally or computationally determined without much difficulty. Although dppe and dppb may have often been shown to be inferior to dppp and dppf, they are included in the list shown above, so as to provide a wider set of structurally related didentate phosphines of various bite angles.

Step 3: Search for new and superior ligands.

Any promising leads gained in *Steps 1 and 2* may then be followed up to come up with new and superior ligands. The scope of such investigations is, however, unlimited.

The three-step protocol presented above may also be applied to the selection of other types of ligands, such as phosphites, amines, and arsines, as well as those centered at C, Si, O, S, and other atoms.

Finally, special requirements, such as Pd-catalyzed asymmetric syntheses (**Sects. II.2.7**, **III.2.16**, **IV.2.3**, and **V.2.4**), water-soluble Pd complexes (**Sect. X.1**), immobilized Pd complexes (**Sect. X.2**), and combinatorial synthesis (**Sect. X.3**), call for the preparation and use of specially designed ligands, as discussed in the sections indicated in parentheses.

REFERENCES

[1] F. J. Mann and D. Purdie, *J. Chem. Soc.*, **1935**, 1549.

[2] J. M. Jenkins and B. L. Shaw, *J. Chem. Soc. (A)*, **1966**, 770.

[3] W. J. Louch and D. R. Eaton, *Inorg. Chim. Acta*, **1978**, *30*, 243.

[4] C. M. Hettrick and W. J. Scott, *J. Am. Chem. Soc.*, **1991**, *113*, 4903.

[5] F. Ozawa, H. Soyama, H. Yanagihara, I. Aoyama, H. Takino, K. Izawa, T. Yamamoto, and A. Yamamoto, *J. Am. Chem. Soc.*, **1985**, *107*, 3235.

[6] W. Kuran and A. Musco, *Inorg. Chim. Acta*, **1975**, *12*, 187.

[7] R. Uson, J. Fornies, and F. Martinez, *J. Organomet. Chem.*, **1977**, *132*, 429.

[8] H. C. Clark and K. R. Dixon, *J. Am. Chem. Soc.*, **1969**, *91*, 596.

[9] J. P. Neilan, R. M. Laine, N. Cortese, and R. F. Heck, *J. Org. Chem.*, **1976**, *41*, 3455.
[10] T. A. Stephenson, S. M. Morehouse, A. R. Powell, J. P. Heffer, and G. Wilkinson, *J. Chem. Soc.*, **1965**, 3632.
[11] M. A. Bennett and P. A. Longstaff, *J. Am. Chem. Soc.*, **1969**, *91*, 6266.
[12] D. R. Coulson, *Inorg. Synth.*, **1972**, *13*, 121.
[13] A. D. Westland, *J. Chem. Soc.*, **1965**, 3060.
[14] D. W. Meek, P. E. Nicpon, and V. I. Meek, *J. Am. Chem. Soc.*, **1970**, *92*, 5351.
[15] W. L. Steffen and G. Palenik, *Inorg. Chem.*, **1976**, *15*, 2432.
[16] A. R. Sanger, *J. Chem. Soc. Dalton Trans.*, **1977**, 1971.
[17] T. Hayashi, M. Konishi, Y. Kobori, M. Kumada, T. Higuchi, and K. Hirotsu, *J. Am. Chem. Soc.*, **1984**, *106*, 158.
[18] A. Gillie and J. K. Stille, *J. Am. Chem. Soc.*, **1980**, *102*, 4933.
[19] E. W. Stern and P. K. Maples, *J. Catal.*, **1972**, *27*, 120.
[20] Y. Ben-David, M. Portnoy, and D. Milstein, *J. Am. Chem. Soc.*, **1989**, *111*, 8742.
[21] Y. Ben-David, M. Portnoy, M. Gozin, and D. Milstein, *Organometallics*, **1992**, *11*, 1995.
[22] G. Peiffer, S. Chhan, A. Bendayan, B. Waegell, and J.-P. Zahra, *J. Mol. Cat.*, **1990**, *59*, 1.
[23] A. L. Casalnuovo and J. C. Calabrese, *J. Am. Chem. Soc.*, **1990**, *112*, 4324.
[24] W. A. Herrmann and C. W. Kohlpaintner, *Angew. Chem. Int. Ed. Engl.*, **1993**, *32*, 1524.
[25] T. Sakakura, H. Yamashita, T. Kobayashi, T. Hayashi, and M. Tanaka, *J. Org. Chem.*, **1987**, *52*, 5733.
[26] L. A. Paquette, D. R. Sauer, D. G. Cleary, M. A. Kinsella, C. M. Blackwell, and L. G. Anderson, *J. Am. Chem. Soc.*, **1992**, *114*, 7375.
[27] T. J. Hutteman, Jr., B. M. Foxman, C. R. Sperati, and J. G. Verkade, *Inorg. Chem.*, **1965**, *4*, 950.
[28] B. M. Trost, T. N. Nanninga, and D. M. T. Chan, *Organometallics*, **1982**, *1*, 1543.
[29] T. Ito, T. Kawai, and Y. Takami, *Tetrahedron Lett.*, **1972**, 4775.
[30] M. Beller and A. Zapf, *Synlett*, **1998**, 792.
[31] J. M. Townsend, I. D. Reingold, M. C. R. Kendall, and T. A. Spencer, *J. Org. Chem.*, **1975**, *40*, 2976.
[32] J. E. Bäckvall, J. O. Vagberg, C. Zercher, J. P. Genêt, and A. Denis, *J. Org. Chem.*, **1987**, *52*, 5430.
[33] J. P. Genêt, J. Uziel, and S. Juge, *Tetrahedron Lett.*, **1988**, *29*, 4559.
[34] Y. Takahashi, T. Ito, S. Sakai, and Y. Ishii, *Chem. Commun.*, **1970**, 1065.
[35] E. Negishi, T. Takahashi, and K. Akiyoshi, *J. Chem. Soc. Chem. Commun.*, **1986**, 1339.
[36] E. Negishi, unpublished results.
[37] J. Tsuji, *Palladium Reagents and Catalysts. Innovations in Organic Synthesis*, Wiley, New York, **1995**, 560 pp.
[38] T. E. Nalesnik and N. L. Holy, *J. Org. Chem.*, **1977**, *42*, 372.
[39] T. F. Blackburn and J. Schwartz, *J. Chem. Soc. Chem. Commun.*, **1977**, 157.
[40] V. Bellosta, R. Benhaddou, and S. Czernecki, *Synlett*, **1993**, 861.
[41] M. E. Kuehne and T. C. Hall, *J. Org. Chem.*, **1976**, *41*, 2742.
[42] T. Mandai, T. Matsumoto, J. Tsuji, and S. Saito, *Tetrahedron Lett.*, **1993**, *34*, 2513.
[43] M. Graziani, P. Uguagliati, and G. Carturan, *J. Organomet. Chem.*, **1971**, *27*, 275.
[44] D. M. Fenton and P. J. Steinwand, *J. Org. Chem.*, **1974**, *39*, 701.
[45] E. Negishi, T. Takahashi, and K. Akiyoshi, *J. Organomet. Chem.*, **1987**, *334*, 181.

[46] A. J. Zapata and A. C. Rondon, *Org. Prep. Proc. Int.*, **1995**, *27*, 567.
[47] V. Farina, S. R. Baker, and C. Sapino, Jr., *Tetrahedron Lett.*, **1988**, *29*, 6043.
[48] V. Farina and B. Krishnan, *J. Am. Chem. Soc.*, **1991**, *113*, 9585.
[49] E. Negishi, Z. R. Owczarczyk, and D. R. Swanson, *Tetrahedron Lett.*, **1991**, *32*, 4453.
[50] E. Negishi, M. Pour, F. E. Cederbaum, and M. Kotora, *Tetrahedron*, **1998**, *54*, 7057.
[51] C. Amatore, A. Jutand, G. Meyer, H. Atmani, F. Khalil, and F. O. Chahdi, *Organometallics*, **1998**, *17*, 2958.
[52] W. Shen, *Tetrahedron Lett.*, **1997**, *38*, 5575.
[53] A. F. Littke and G. C. Fu, *Angew. Chem. Int. Ed. Engl.*, **1998**, *37*, 3387.
[54] J. P. Wolfe and S. L. Buchwald, *Angew. Chem. Int. Ed. Engl.*, **1999**, *38*, 2413.
[55] A. F. Littke and G. C. Fu, *J. Org. Chem.,* **1999**, *64*, 10.
[56] A. F. Littke and G. C. Fu, *Angew. Chem. Int. Ed. Engl.*, **1999**, *38*, 2411.
[57] J. M. Brown and P. J. Guiry, *Inorg. Chim. Acta*, **1994**, *220*, 249.
[58] M. Rottländer and P. Knochel, *J. Org. Chem.*, **1998**, *63*, 203.
[59] M. Kranenburg, P. C. J. Kamer, and P. W. N. M. van Leeuwen, *Eur. J. Inorg. Chem.*, **1998**, 155.
[59a] P. W. N. M. van Leeuwen, P. C. J. Kamer, J. N. H. Reek, and P. Dierkes, *Chem. Rev.*, **2000**, *100*, 2741–2769.
[60] B. C. Hamann and J. F. Hartwig, *J. Am. Chem. Soc.*, **1997**, *119*, 12382.
[61] B. C. Hamann and J. F. Hartwig, *J. Am. Chem. Soc.*, **1998**, *120*, 3694.
[62] J. F. Hartwig, *Angew. Chem. Int. Ed. Engl.*, **1998**, *37*, 2046.
[63] J. A. Miller and R. P. Farrell, *Tetrahedron Lett.*, **1999**, *39*, 6441.
[64] J. A. Miller and R. P. Farrell, *Tetrahedron Lett.*, **1999**, *39*, 7275.
[65] G. Mann, D. Baranano, J. F. Hartwig, A. L. Rheingold, and I. A. Guzei, *J. Am. Chem. Soc.*, **1998**, *120*, 9205.
[66] F. Paul, J. Patt, and J. F. Hartwig, *J. Am. Chem. Soc.*, **1994**, *116*, 5969.
[67] J. F. Hartwig and F. Paul, *J. Am. Chem. Soc.*, **1995**, *117*, 5373.
[68] S. Otsuka, T. Yoshida, M. Matsumoto, and K. Nakatsu, *J. Am. Chem. Soc.*, **1976**, *98*, 5850.
[69] C. Amatore, M. Azzabi, and A. Jutand, *J. Am. Chem. Soc.*, **1991**, *113*, 8375.
[70] J. P. Collman, L. S. Hegedus, J. R. Norton, and R. G. Finke, *Principles and Applications of Organotransition Metal Chemistry*, 2nd ed., University Science Books, Mill Valley, CA, **1987**, 989 pp.
[71] M. Kotora and E. Negishi, *Synthesis*, **1997**, 121.
[72] G. B. Kauffman and J. H.-S. Tsai, *Inorg. Synth.*, **1966**, *8*, 234.
[73] F. R. Hartley, S. G. Murray, and C. A. McAuliffe, *Inorg. Chem.*, **1979**, *18*, 1394.
[74] A. Sen, T.-W. Lai, and R. R. Thomas, *J. Organomet. Chem.*, **1988**, *358*, 567.
[75] J. R. Doyle, P. E. Slade, and H. B. Jonassen, *Inorg. Synth.*, **1960**, *6*, 216.
[76] F. R. Hartley, *Organomet. Chem. Rev. A*, **1970**, *6*, 119.
[77] B. J. McCormick, E. N. Jaynes, Jr., and R. I. Kaplan, *Inorg. Synth.*, **1972**, *13*, 216.
[78] D. A. Baldwin and G. J. Leigh, *J. Chem. Soc. (A)*, **1968**, 1431.
[79] T. N. Hazarika, *Asian J. Chem.*, **1992**, *4*, 179.
[80] R. van Asselt and C. J. Elsevier, *Organometallics*, **1994**, *13*, 1972.
[81] A. Sen and T.–W. Lai, *J. Am. Chem. Soc.*, **1981**, *103*, 4627.
[82] R. van Asselt, C. J. Elsevier, W. J. J. Smeets, and A. L. Spek, *Inorg. Chem.*, **1994**, *33*, 1521.
[83] G. G. Wu, Y.-S. Wong, and M. Poirier, *Org. Lett.*, **1999**, *1*, 745.
[84] R. van Asselt, K. Vrieze, and C. J. Elsevier, *J. Organomet. Chem.*, **1994**, *480*, 27.

[85] B. A. Markies, A. J. Canty, W. de Graaf, J. Boersma, M. D. Janssen, M. P. Hogerheide, W. J. J. Smeets, A. L. Spek, and G. van Koten, *J. Organomet. Chem.*, **1994**, *482*, 191.

[86] P. Ramiandrasoa, B. Bréhon, A. Thivet, M. Alami, and G. Cahiez, *Tetrahedron Lett.*, **1997**, *38*, 2447.

[87] M. Alami and F. Ferri, *Synlett*, **1996**, 755.

[88] A. M. Castaño, M. Ruano, and A. M. Echavarren, *Tetrahedron Lett.*, **1996**, *37*, 6591.

[89] R. van Asselt and C. J. Elsevier, *J. Mol. Cat.*, **1991**, *65*, L13.

[90] B. M. Trost and D. J. Jebaratnam, *Tetrahedron Lett.*, **1987**, *28*, 1611.

[91] R. Sustmann, J. Lau, and M. Zipp, *Tetrahedron Lett.*, **1986**, *27*, 5207.

[92] R. van Asselt and C. J. Elsevier, *Tetrahedron*, **1994**, *50*, 323.

[93] B. Akermark, S. Hansson, and A. Vitagliano, *J. Am. Chem. Soc.*, **1990**, *112*, 4587.

[94] R. E. Rülke, D. Kliphuis, C. J. Elsevier, J. Fraanje, K. Goubitz, P. W. N. M. van Leeuwen, and K. Vrieze, *J. Chem. Soc. Chem. Commun.*, **1994**, 1817.

[95] E. Shirakawa, H. Yoshida, and H. Takaya, *Tetrahedron Lett.*, **1997**, *38*, 3759.

[96] E. Shirakawa, H. Yoshida, T. Kurahashi, Y. Nakao, and T. Hitama, *J. Am. Chem. Soc.*, **1998**, *120*, 2975.

[97] E. Shirakawa, H. Yoshida, and T. Hiyama, *Tetrahedron Lett.*, **1997**, *38*, 5177.

[98] D. W. Old, J. P. Wolfe, and S. L. Buchwald, *J. Am. Chem. Soc.*, **1998**, *120*, 9722.

[99] E. Drent, P. Arnoldy, and P. H. M. Budzelaar, *J. Organomet. Chem.*, **1994**, *475*, 57.

[100] M. T. Reetz, R. Demuth, and R. Goddard, *Tetrahedron Lett.*, **1998**, *39*, 7089.

[101] L. Malatesta and M. Angoletta, *J. Chem. Soc.*, **1957**, 1186.

[102] W. Levason and C. A. McAuliffe, *J. Chem. Soc. Dalton Trans.*, **1974**, 2238.

[103] T. Kobayashi and M. Tanaka, *J. Organomet. Chem.*, **1981**, *205*, C27.

[104] B. M. Trost, E. D. Edstrom, and M. B. Carter-Petillo, *J. Org. Chem.*, **1989**, *54*, 4489.

[105] E. Negishi, T. Takahashi, S. Baba, D. E. Van Horn, and N. Okukado, *J. Am. Chem. Soc.*, **1987**, *109*, 2393.

[106] V. Farina and G. P. Roth, *Tetrahedron Lett.*, **1991**, *32*, 4243.

[107] V. Farina, B. Krishnan, D. R. Marshall, and G. P. Roth, *J. Org. Chem.*, **1993**, *58*, 5434.

[108] A. L. Casado and P. Espinet, *J. Am. Chem. Soc.*, **1998**, *120*, 8978.

[109] R. Faust and B. Göbelt, *J. Prakt. Chem.*, **1998**, *340*, 90.

[110] T. Watanabe, N. Miyaura, and A. Suzuki, *J. Organomet. Chem.*, **1993**, *444*, C1.

[111] T. Ahiko, T. Ishiyama, and N. Miyaura, *Chem. Lett.*, **1997**, 811.

[112] A. Pimm, P. Kocienski, and S. D. A. Street, *Synlett*, **1992**, 886.

[113] A. Godt, *J. Org. Chem.*, **1997**, *62*, 7471.

[114] R. Rossi, F. Bellina, A. Carpita, and R. Gori, *Synlett*, **1995**, 344.

[115] S.-K. Kang, E.-Y. Namkoong, and T. Yamaguchi, *Synth. Commun.*, **1997**, *27*, 641.

[116] S. Gagneur, H. Makabe, and E. Negishi, *Tetrahedron. Lett.*, **2001**, *42*, 785.