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Phosphapalladacycles: preparation routes †

V V Dunina, O N Gorunova

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Abstract. The review considers methods of synthesis of cyclopalladated compounds of the PC- and PCP-type including intramolecular activation of the C–H bonds in the P-donor ligands, oxidative addition of preliminarily functionalised substrates to palladium(0), transmetallation of lithiated compounds, chelation of phosphine-substituted phosphorus ylides, and some non-standard processes resulting in a new ligand formation on a metal template. Particular attention has been given to the structural factors and experimental conditions that determine the feasibility of direct cyclopalladation of mono- and bidentate phosphines, phosphites and phosphinites. The bibliography includes 384 references.

I. Introduction

A driving force for writing of this review was the impressive progress achieved in the modern homogeneous metal complex catalysis due to the use of metallacycles as catalysts or precatalysts.[1–5] A pronounced increase in the catalytic activity due to *ortho*-metallation (for phosphites) was first detected by Lewis in 1986.[6,7] The unique role of phosphine complexes of palladium in classical homogeneous catalysis is known; therefore, it is not surprising that phosphapalladacycles occupy a central place in the new branch of catalysis.[1,5,8–12]

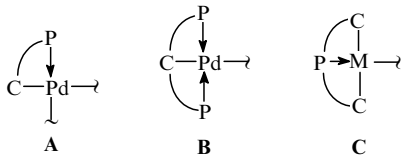
Some data concerning the chemistry of mono- and bicyclic compounds of this class, including their dendrimeric forms,[13] can be found in recent reviews dealing with cyclometallation (involving all metals [14–20] or only palladium [21]) and organopalladium compounds.[22] Among the survey papers devoted to cyclometallated structures each with one particular heterodonor atom,[19,23–28] only one publication [19] is known dealing with complexes of various metals with P-donor ligands (up to mid-1979). The monograph by Omae,[18] which summarises his earlier reviews is largely a compilation (as noted in a book review [29]).

V V Dunina, O N Gorunova Department of Chemistry, M V Lomonosov Moscow State University, Leninskie Gory, 119992 Moscow, Russian Federation. Fax (7-095) 932 88 46. Tel. (7-095) 939 53 76.
E-mail: dunina@org.chem.msu.ru (V V Dunina), o.gorunova@org.chem.msu.ru (O N Gorunova)

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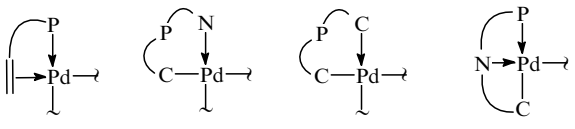
The intensive development of this field seen in recent years calls for a deliberate consideration of the existing routes to phosphapalladacycles known to date (up to the end of 2002) and elucidation of the specific features of the process of their formation.

The purpose of this review is to analyse the methods of synthesis of cyclopalladated complexes with P-donor atoms with the emphasis on the factors that determine the feasibility of this process. The reactions of phosphapalladacycles will be considered elsewhere. Compounds in which the metal is linked directly to one or two phosphorus(III) atoms and to one carbanionic centre incorporated in an anionic bi- or tridentate chelating ligand (mono- or bicyclic structures of kind **A** or **B**) were chosen as the objects. Optically active compounds of this type constitute the subject of a special review. Type **C** structures for palladium have not been obtained as yet, although for other transition metals (for example, Rh, Ir and Pt), not only CPC- [30,31] but also PCPC- [32] and PCCP-type complexes are known.[33]



A **B** **C**

Compounds of structural types **D** – **G** are beyond the scope of this review, because their properties differ appreciably from those typical of classical mono- or dianionic phosphapalladacyclic systems. These include compounds with phosphines chelated to the metal due to additional π-coordination through their double bonds (**D**);[34–39] metallacycles of other types, for example, CN- (**E**) [40,41] or CC-types (**F**),[41–45] containing a non-donor phosphorus atom; and bicyclic structures with the Pd–C and Pd←P bonds located in two different metallacycles (*e.g.*, those of **G** type).[46,47]



D **E** **F** **G**

† The first review in a series of publications devoted to the chemistry and stereochemistry of phosphapalladacycles.

Conversely, PC-chelated phosphine-substituted phosphorus ylides are covered in the review, despite the formally neutral character of these ligands (actually, they are zwitter-ionic), because their C-donor atom shows carbanionic properties. Dendrimers containing phosphapalladacycles[13] are not discussed, but their precursors[48–50] are included in Tables 1–4 (see Supplement).

The basic difference between metallacyclic systems with P-heterodonor atoms and their CN- or NCN-analogues is that the phosphorus atom can act not only as a σ-donor but also as a π-acceptor.[51–54] Many other properties of phosphapalladacyclic systems account for the fact that they are considered separately. These include the higher atomic radius of phosphorus, the lower basicity and greater 'softness' of this atom (the latter is especially important for the complexation with the 'soft' palladium atom) and much higher strength of the P → Pd bonds compared to the N → Pd bonds. Since the possibility of structural modification aimed at the optimisation of electronic and steric characteristics of the metal and its environment is extremely important for almost any field of application of cyclopalladated complexes, the demand for information on the synthetic routes to these compounds is evident.

An idea of the diversity of known phosphapalladacyclic compounds can be gained from Tables 1–4 given in the Supplement, which summarise methods for the synthesis of complexes classified in terms of structural features. Monochelate compounds of the PC-type (**A**) and their bicyclic or 'pincer' PCP analogues (**B**) are included in Tables 1 and 4, respectively; the bis(chelate) spiro complexes and derivatives of PC-coordinated phosphine-substituted phosphorus ylides are considered in Tables 2 and 3, respectively. The Tables give only the structures of primary cyclometallation products arranged according to the type of hybridisation of the metal-bound carbon atom (sp^3 or sp^2) and to the size of the chelate ring formed (six-, five- or four-membered). The reaction conditions, the types of intermediates (for multistage processes), the yields in the stage of cyclometallation itself and the total yield (for multistage routes) are also presented.

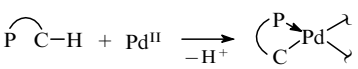
In the text and in the Tables, the ordinal number of the complex corresponds to the superscript in the designation of the cyclopalladated ligand HL^n, while letters designate all compounds derived from this ligand; the numbers of similar complexes of other metals are primed.

While Tables 1–4 can be useful for the synthesis of known complexes, the main goal of the discussion of published data is to elucidate the regular trends which could be useful for the design of new phosphapalladacycles and in the search for methods for their synthesis.

The routes to cyclopalladated complexes with P-donor atoms are diverse, the most important being direct activation of C–H bonds (Section II) and oxidative addition of a C–H or C–Hal bond of the ligand to a low-valence metal (Section III). Other possible approaches include complexation of Pd(II) with a prelithiated ligand (transmetallation, Section IV) or its simple chelation by formally neutral phosphine-substituted phosphorus ylide ligands (Section V). Some exotic transformations resulting in closure of phosphapalladacycles are considered in Section VI.

II. Direct intramolecular cyclopalladation

Direct intramolecular activation of C–H bonds in P-donor ligands seems to be the most attractive route to phosphapalladacycles.



The efficiency of this method is determined, first of all, by the ligand structure; if necessary, it can be increased by optimisation of the reaction conditions. This Section is devoted to consideration of these factors.

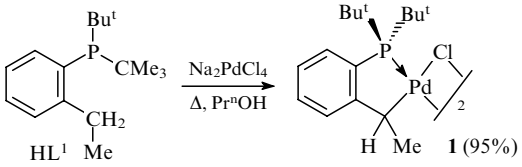
1. Structural factors

The ease of cyclopalladation of a P-donor ligand depends, first of all, on its structural features including the position of the C–H bond to be activated (this dictates the size of the phosphapalladacycle formed) and hybridisation of the carbon atom involved, the steric conditions near the P-donor atom and near the metallation site, the basicity of phosphorus atom, *etc*.

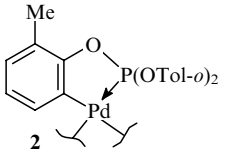
a. Localisation of the C–H bond to be activated

The position of the C–H bond being activated with respect to the P-donor atom largely determines the ease of cyclopalladation: the tendency for the formation of five-membered PC-palladacycles is as pronounced as in the case of ligands with other donor atoms.[21]

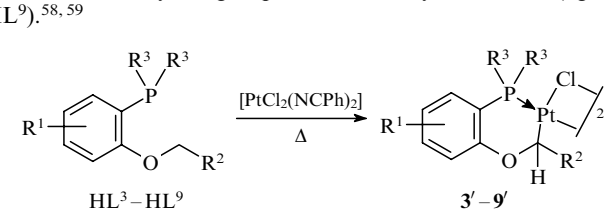
For example, phosphine HL^1 forms only a five-membered metallacycle in complex **1** due to the activation of the C–H bond of the methylene group in the *o*-Et substituent,[55] despite the presence of aliphatic C–H bonds in sterically less hindered methyl groups of the *o*-Et and PBu^t substituents and an aromatic C–H bond whose activation could have resulted in six- or four-membered metallacycles. The reactions with other aryl-, benzyl- and alkyl-phosphines with PBu^t substituents also always lead to the closure of five-membered palladacycles (see Table 1).



The same trend becomes apparent in Pd(II) reactions with phosphites. Cyclopalladation of tri(*o*-tolyl) phosphite (HL^2) both *via* the standard coordination precursor, $[Pd(\kappa^1\text{-}HL^2)_2Cl_2]$,[56] and *via* the organometallic compound, $[PdCl(\eta^5\text{-}Cp)(HL^2)]$,[57] affords only the five-membered palladacycle **2** due to the attack by palladium on the benzene ring, although the formation of a six-membered metal ring is also possible in principle through activation of the *o*-Me group of the tolyl substituent.



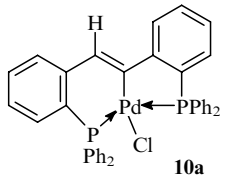
The six-membered metallacycles are rather uncommon; their formation is hampered and becomes possible only when there are no alternatives. For instance, all attempts to close six-membered PC-palladacycles upon activation of the $C(sp^3)$–H bond in the *o*-AlkO group of the phosphines HL^3–HL^9 failed, even in the case of sterically hindered HL^4, HL^6 and HL^8 ligands. It is noteworthy that the corresponding platinacycles **3′**–**9′** are formed upon metallation of not only the methyl group (ligands HL^3–HL^8) but also the methylene group of the *o*-alkoxy substituent (ligand HL^9).[58, 59]



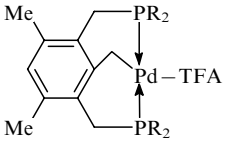
$R^1 = R^2 = H$: $R^3 = Ph$ (HL^3, **3′**), Bu^t (HL^4, **4′**);
$R^1 = 3\text{-MeO}$, $R^2 = H$: $R^3 = Ph$ (HL^5, **5′**), Bu^t (HL^6, **6′**);
$R^1 = 6\text{-MeO}$, $R^2 = H$: $R^3 = Ph$ (HL^7, **7′**), Bu^t (HL^8, **8′**);
$R^1 = H$, $R^2 = Me$, $R^3 = Ph$ (HL^9, **9′**).

As rare examples of six-membered phosphapalladacycles, one can mention bicyclic PCP structures **10a**, **11** and **12**, prepared from

2,2′-bis(diphenylphosphino)stilbene (HL^{10})[60,61] and 1,3-bis-(phosphinomethyl)-2,4,6-trimethylbenzenes (HL^{11} and HL^{12}).[62] In the case of complex **10a** and related derivatives of diphosphines with the dibenzyl skeleton (see Table 4), the unfavourableness of the formation of a six-membered chelate ring is partially compensated by the simultaneous closure of the optimal five-membered phosphapalladacycle.



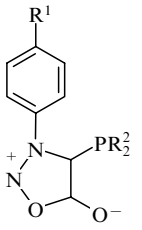
10a



11 (R = Pr^i), **12** (R = Bu^t)

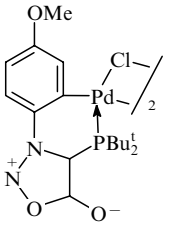
TFA is trifluoroacetate.

The only example of formation of a six-membered PC-palladacycle by a monodentate ligand is *ortho*-palladation of 4-(di-*tert*-butylphosphino)-3-(4-methoxyphenyl)sydnone (HL^{13}). The structure of dimer **13** was confirmed by X-ray diffraction.[63]



HL^{13}–HL^{16}

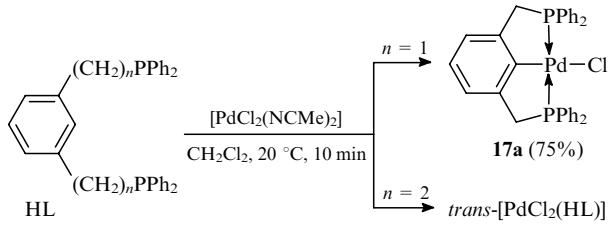
Ligand	R^1	R^2
HL^{13}	MeO	Bu^t
HL^{14}	H	Bu^t
HL^{15}	MeO	Ph
HL^{16}	H	Ph



13

The *ortho*-palladation of sydnonylphosphine HL^{13} is possible only under simultaneous assistance of steric and electronic factors. Studies of other ligands of this class have shown that in the absence of the electron-donating 4-MeO group in the aromatic ring but with retention of the bulky substituents at phosphorus (HL^{14})[64] and, especially, upon replacement of the bulky PBu^t_2 group by the less bulky PPh_2 fragment in ligands HL^{15} (see Ref. 65) and HL^{16} (see Ref. 64), the reaction under the same conditions ($PdCl_2$–HCl, EtOH–H_2O, 80 °C, 4 h) gives simple coordination complexes of the type *trans*-[$PdCl_2(HL)_2$], instead of *ortho*-palladated compounds.

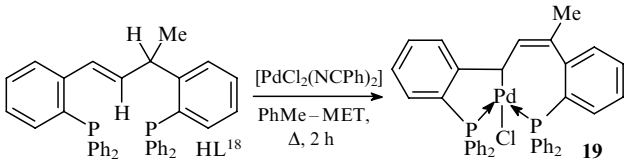
It is equally obvious that the formation of five-membered metallacycles in the case of PCP-complexes is facilitated. Unlike *m*-xylylene-α,α′-diphosphine (HL^{17}, $n = 1$), which is easily cyclopalladated under mild conditions (CH_2Cl_2, 20 °C) to give bicyclic structure **17a** with five-membered metallacycles,[66] its homologue with longer diatomic ($n = 2$) bridges between the PPh_2 groups and the phenylene skeleton cannot be involved in this process. Under the same and even under more rigorous conditions, it affords only a coordination complex of the *trans*-[$PdCl_2(HL)$] type with P,P-chelated diphosphine.[67]



HL

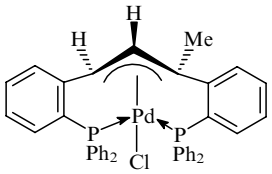
$n = 1$ (HL^{17}), 2.

A forcible argument in favour of the preferred formation of five-membered phosphapalladacycles may be derived from the results of palladation of diphosphine HL^{18}. Despite the potential possibility of closure of two six-membered metal rings with participation of the C(sp^2)–H vinyl bond, a PCP-structure **19** with five- and seven-membered palladacycles is formed upon the formal 1,2-migration of the double bond in the ligand (as confirmed by X-ray diffraction).[68]



MET is 2-methoxyethanol.

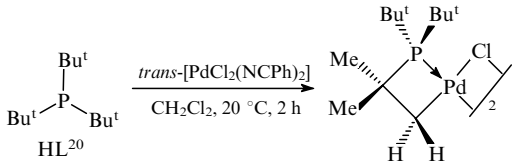
Presumably, the reaction includes the formation of cationic η^3-allylic intermediate **A** upon deprotonation of the tertiary carbon atom of the ArC(Me)H fragment whose C–H bond is most 'acidified', due to its simultaneously benzylic and allylic positions.



A

The formation of intermediate **A** was confirmed by isolation of its tetrafluoroborate upon dehalogenation of complex **19** under the action of $AgBF_4$. The driving force of subsequent rearrangement of intermediate **A** to the η^1-allylic structure **19** is minimisation of steric strain in the tetracyclic system consisting of two metallacycles and two aromatic rings.[68] This factor appears to be even more important in view of the fact that in the case of diphosphine ligands, the activation of the C(sp^2)–H bonds is usually preferred over the activation of the C(sp^3)–H bond and occurs much more easily (see below).

The closure of the four-membered metallacycle upon cyclopalladation of tri-*tert*-butylphosphine (HL^{20}) is also forced, as this ligand does not contain any C–H bonds suitable for the formation of five-membered rings.[69–74]



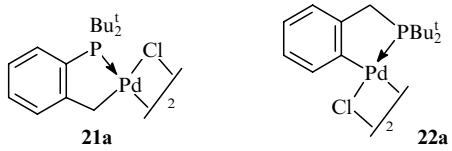
20a (70%)

Probably, the formation of these sterically 'inconvenient' metallacycles is facilitated by the rather large bulk of the phosphorus atom; to some extent, this is also stimulated by steric effects of P-substituents[75] (see below). It should be noted that, in spite of the smaller atomic radius of nitrogen, compounds with four-membered CN-palladacycles are also encountered, although rather seldom;[40,76–78] they are mainly formed with dianionic ligands[77,78] and are prone to ring expansion.[79]

b. Hybridisation of the metallated carbon

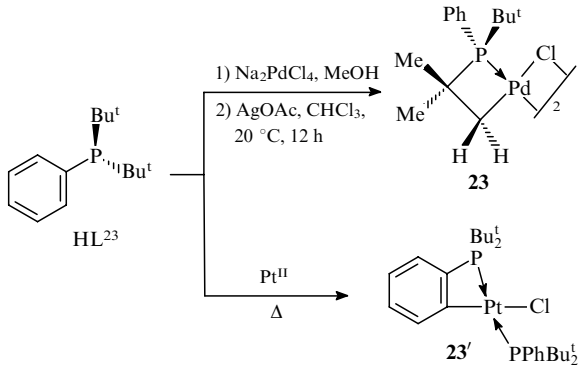
The hybridisation of the carbon atom in the C–H bond being metallated undoubtedly influences the ease of cyclometallation. Formal considerations concerning different strengths of aromatic and aliphatic C–H bonds (with an energy of ~110 and ~100 kcal mol^{-1}, respectively[80]) are of little utility due to the complex combination of various factors determining the course of this process (thermodynamics and kinetics, mechanistic features, steric effects, and so on). However, analysis of the available experimental results indicates that the hybridisation of carbon in the C–H bond that is metallated plays different roles in PC- and PCP-systems.

Comparison of the formation conditions of five-membered PC-palladacycles **21a** and **22a** from di-*tert*-butyl-substituted phosphines P(Tol-*o*)Bu^t_2 (HL^{21}) (Na_2PdCl_4, MeOH – PrOH, ~60 °C, 5 min, 90%) and $PBnBu^t_2$ (HL^{22}) (Na_2PdCl_4, MET, 125 °C, 5 days, 64%) shows that the C(sp^3) – H bond in the former ligand [81] is activated more readily than the C(sp^2) – H bond in the latter ligand,[82] as in the first case the reaction requires much less time and occurs at a lower temperature, the dimer being formed in a higher yield.



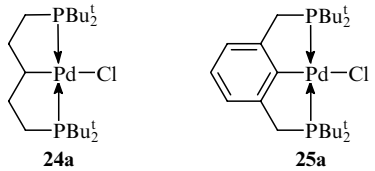
21a **22a**

This regularity is also retained in systems with four-membered metallacycles. Indeed, the bond to be activated during the cyclopalladation of the phosphine $PPhBu^t_2$ (HL^{23}) is the aliphatic C – H bond of the *tert*-butyl group [83,84] rather than the aromatic *o*-C – H bond of the P-phenyl substituent. The lower steric promotion required the use of silver acetate for halide abstraction in this process.



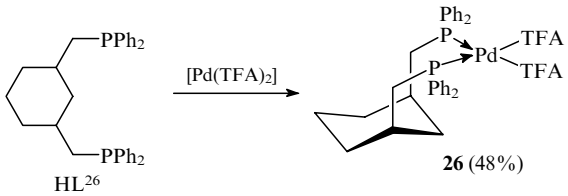
It should be noted that cycloplatination of the HL^{23} ligand and related phosphines follows an opposite trend, *i.e.*, the aromatic C – H bond is attacked preferably to give *ortho*-metallated platinum complex **23′**.[85–87] Moreover, measurements of the H/D exchange kinetics showed that in the presence of platinum(II), the exchange rate of *ortho*-protons in the PPh substituent of phosphine HL^{23} is 50 times as high as the exchange rate of protons in the PBu^t groups.[88] Palladium(II) compounds with four-membered phosphametallacycles, like complex **23′**, have been prepared by a different method (see Section III).

The opposite trend is observed in the formation of two related PCP-complexes, **24a** (260 °C, sublimation, 64%) [89] and **25a** (MET, 125 °C, 25 min, 75%),[90] in the reaction of diphosphines with the same reagent, [$PdCl_2(NCPh)_2$]. Namely, the activation of the aliphatic C – H bond requires higher temperature [or the use of a more efficient reagent, palladium(II) trifluoroacetate [91]] than the palladation involving the aromatic C – H bond.

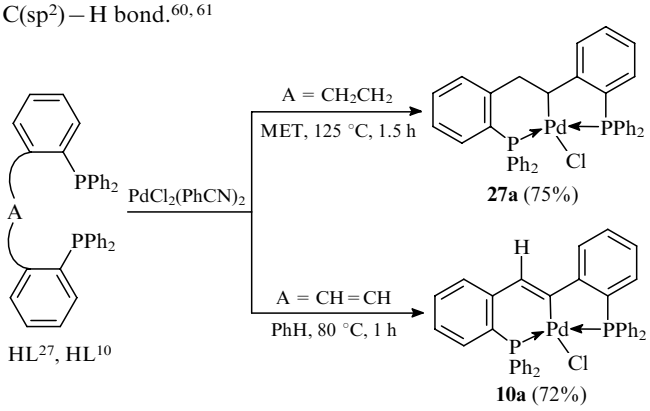


24a **25a**

This difference is even more pronounced in similar, but sterically non-crowded systems with PPh_2 donor groups. Of two diphosphines, one with a *m*-xylylene (HL^{17}) [66] and one with a fully hydrogenated *cis*-cyclohexane-1,3-dimethylene skeleton (HL^{26}),[92] only the former can be effectively palladated at the C(sp^2) – H bond under very mild conditions under the action of a mild reagent, [$PdCl_2(NCMe)_2$], whereas the latter forms only the coordination complex **26** even when treated with the more electrophilic palladium(II) trifluoroacetate.



A similar, although less pronounced trend is found in cyclopalladation of the pair of diphosphines with dibenzyl (HL^{27}) or stilbene (HL^{10}) bridges: the activation of the C – H aliphatic bond in the former one requires longer-term refluxing in a more basic solvent (MET) than metallation of the latter HL^{10} ligand at the C(sp^2) – H bond.[60,61]



A = CH_2CH_2 (HL^{27}), *trans*-CH=CH (HL^{10}).

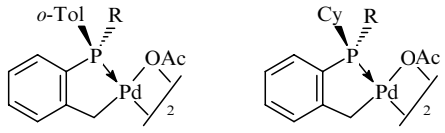
In support of the structure of the complex **10a**, X-ray data for the platinum analogue can be mentioned.[60,93] The mechanism of cyclometallation of two related ligands, HL^{27} and HL^{10}, has not been studied; however, it was suggested that activation of the C(sp^2) – H bond in diphosphine HL^{10} can be facilitated due to the formation of an ionic intermediate with a π-coordinated double bond.[61]

Cyclopalladation involving the C(sp^3) – H bond does not take place for diphosphine (2-$Ph_2PC_6H_4)_2CH_2$ (HL^{28}) with the diphenylmethane skeleton containing PPh_2 donor groups. Refluxing of the HL^{28} ligand with [$PdCl_2(NCPh)_2$] furnishes only the coordination complex *cis*-[$PdCl_2(HL^{28})$], despite the potential possibility of the closure of two optimal five-membered phosphapalladacycles.[94]

Thus, for mono- and diphosphine ligands, the ease of cyclopalladation follows opposite patterns of dependence on the type of hybridisation of the carbon atom in the C – H bond that is activated. This suggests that the reaction routes, resulting in the PC- and PCP-structures may be different.

c. The basicity of the phosphorus donor atom

Theoretically, the process rate can also be influenced by the basicity and the coordination ability of the donor atom of phosphorus [51–53] due to the change in the electron density on the metal atom in the coordination precursors. However, comparison of the results of cyclopalladation with palladium(II) acetate of two pairs of *o*-tolylphosphines (HL^{29}, HL^{30} and HL^{31}, HL^{32}) differing in the nature of two other substituents at the phosphorus atoms shows that these factors are relatively insignificant.



29a, **30a** **31**, **32**

Compound	R	θ /deg	Reaction conditions	Yield (%)
29a	*o*-Tol	194	50 °C, 3 min	93
30a	Bu^t	190	60 °C, 5 min	94
31	*o*-Tol	186	20 °C, 6 h	42
32	Cy	178	20 °C, 12 h	41

Indeed, when the aromatic *o*-tolyl group at the phosphorus atom is replaced by an aliphatic group [Bu^t or cyclohexyl (Cy)], the ligand basicity should substantially increase; this follows from the fact that aliphatic phosphines PBu^t_3 and PCy_3 are much more basic (pK_a 11.4 and 9.70, respectively) than the analogous aromatic phosphine P(Tol-*o*)$_3$ (pK_a 3.08).[52,53] Nevertheless, the activation of the C–H bond is hampered only slightly within any of the above pairs with similar steric characteristics, and the yields of complexes remain almost the same.[10] A decrease in the yield of the cyclopalladated complex on passing from the first pair of complexes to the second one (~90% and ~40%) may be related to both the lower temperatures used in the synthesis and, to some extent, to steric effects, which are measured in terms of the Tolman cone angles (θ) ‡ of the starting phosphines.[95]

d. Steric promotion

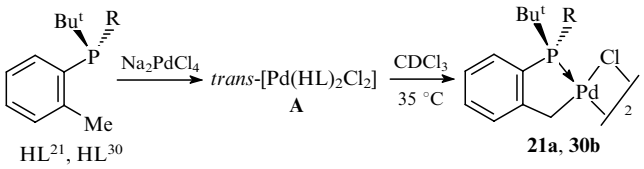
It is in phosphine substrates that the steric promotion of the activation of C–H bonds was first observed by Shaw and coworkers.[85,96,97] This phenomenon has developed into a potent tool in cyclometallation chemistry, which is actively applied to ligands with other heteroatoms, for example, to N-donors.[98–101] Since a phosphorus atom is larger than a nitrogen atom, the steric promotion of reactions of P-donor substrates requires the introduction of more bulky substituents: for example, *tert*-butyl or *o*-tolyl groups are desirable for phosphines, whereas for cyclometallation of benzylamines, it is sufficient to introduce *N*-methyl groups.[21,102] This effect has acquired the name of the *gem*-di-*tert*-butyl effect,[97] by analogy with the Thorpe–Ingold *gem*-dimethyl effect, known from the organic chemistry of small carbocycles.[103–105]

The nature of the steric promotion of cyclometallation processes is rather complex (see Section II.3) and the result is not always predictable. The steric crowding of the P-donor ligands ensures acceleration of the process only for some types of substrate and only for a definite location of bulky substituents.

Most often, bulky substituents at phosphorus markedly facilitate the activation of aromatic and aliphatic C–H bonds in monodentate phosphines, these effects being usually correlated with the Tolman angles of the ligands.[95,106,107] A classical example is the extremely easy closure of a strained four-membered metallacycle in complex **20a** in the reaction of bulky tri(*tert*-butyl)phosphine (HL^{20}) with weak palladating reagents, K_2PdCl_4 or *trans*-[$PdCl_2(NCPh)_2$], at room temperature.[69–71]

The accumulation of *tert*-butyl groups at phosphorus facilitates also the closure of five-membered PC-palladacycles. Spectroscopic (^{1}H NMR) monitoring of formation of cyclopalladated complexes **21a** and **30b** from the corresponding coordination compounds *trans*-[$PdCl_2(HL)_2$] with *o*-tolylphosphines HL^{21} and HL^{30} has shown that in the case of the di-*tert*-butyl-substituted ligand HL^{21}, the reaction is complete in 85 min (yield 100%), whereas with the mono-*tert*-butyl-substituted ligand HL^{30}, one-third of the intermediate coordination complex **A** remain intact even after 5 h.[81]

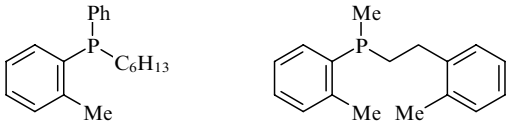
‡ Here and below, the θ values were taken from Ref. 95.



HL^{21}, HL^{30} **A** **21a**, **30b**

R = Bu^t (HL^{21}, **21a**), *o*-Tol (HL^{30}, **30b**).

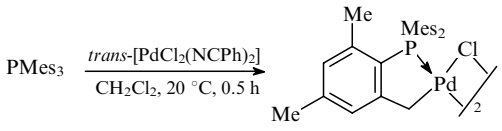
Ligands of the $PRBu^t_2$ type incorporated in coordination precursors such as [$PdCl_2(HL)_2$] often undergo spontaneous cyclometallation even when the latter are kept at room temperature in solution (R = Bu^t)[70] or on attempted recrystallisation (R = 2-EtC_6H_4).[55] Thus, it is quite clear why all attempts at cyclopalladation of the *o*-tolylphosphines HL^{33} and HL^{34} with small substituents at the phosphorus atom have failed.[108]



HL^{33} ($\theta \approx 157°$) HL^{34} ($\theta \approx 148°$)

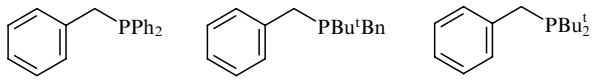
Neither the use of Li_2PdCl_4 and $Pd(OAc)_2$ as palladating agents in the presence of bases (AcONa or K_2CO_3) or without any bases, nor thermolysis (up to 160 °C) of the intermediate coordination complexes [$Pd(HL^{33})_2Hal_2$] or [{$Pd(HL^{34})Hal(\mu\text{-}Hal)$}$_2$], nor even generation of a vacant coordination site in the latter complex on treatment with $AgBF_4$ (see Ref. 108) have led to the desired palladacycles.

Perhaps, steric effects are the most pronounced in the cyclometallation of trimesitylphosphine (HL^{35}).[10,109–111] X-Ray diffraction studies of this bulky ligand (θ = 212 °) have shown that repulsion of the three encumbered mesityl groups results in substantial flattening of the pyramidal configuration at phosphorus, in particular, the angles between the P–C bonds are increased to 108–111 ° compared to the typical values for acyclic phosphines being equal to 90–104 °.[112] Cyclopalladation of this phosphine proceeds under mild conditions, the contribution of the steric promotion being so high that variation of reaction conditions including the solvent (CH_2Cl_2, PhH, $CHCl_3$ or EtOH) and the metal : ligand ratio (1 : 2 or 1 : 1) has virtually no influence on the yields of dimer **35a**, which remain nearly quantitative (87%–98%) in reactions carried out at ~20 °C.[110] The ^{1}H NMR monitoring of the reaction presented below has shown that the process is really over after as soon as 5 min.[109]



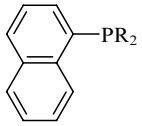
35a (98%)

A similar dependence on the bulk of the P-substituents is also observed in activation of the C(sp^2)–H bonds in benzylphosphines.[82,113,114] The HL^{36} ligand could be cyclometallated with moderate success only using highly electrophilic $Pd(OAc)_2$ (the yield of the dimer was 19%).[114] The intramolecular metallation with a weak electrophile such as Na_2PdCl_4 (AcONa, MET, 130 °C) becomes possible with appearance of the first Bu^t group and is essentially facilitated after the introduction of the second Bu^t group. Thus, the *ortho*-palladated derivatives of the phosphines HL^{37} and HL^{22} are formed in 12% and 75% yields over periods of 24 and 0.5 h, respectively.[82]



HL^{36} (θ = 151°) HL^{37} (θ = 161°) HL^{22} (θ = 177°)

Apparently, it is due to the lack of bulky P-substituents that the attempts to prepare phosphapalladacycles from dimethylnaphthalen-1-ylphosphine (HL^{38}) have not met with success. Neither pyrolysis of the intermediate coordination complexes of the *cis*-$[Pd(HL^{38})_2X_2]$ type (X = Cl, Br) nor long-term refluxing of their solutions in the presence of bases resulted in activation of the $C(sp^2)-H$ bond.[115]

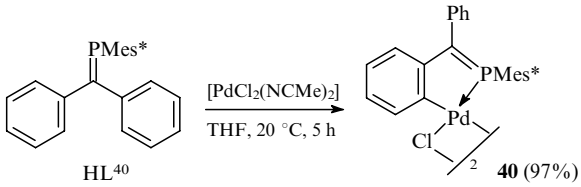


R = Me (HL^{38}), 1-Np (HL^{39});
Np is naphthyl.

HL^{38}, HL^{39}

However, a similar but more bulky tri(naphthalen-2-yl)phosphine (HL^{39}) is cyclometallated on treatment with a more electrophilic reagent, $Pd(OAc)_2$.[116] A certain contribution to increasing the reactivity may also be made by the lower basicity of the P-donor centre in HL^{39} compared to that in HL^{38}.

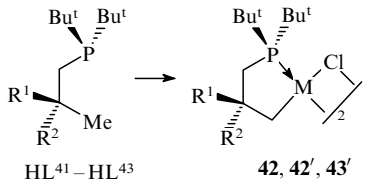
In substrates with P-donor atoms of other types, *ortho*-palladation also proceeds more readily when steric stimulation is involved. For instance, monodentate phosphaalkenes with an extremely bulky 'supermesityl' substituent (Mes* = 2,4,6-$Bu^t_3C_6H_2$) form phosphapalladocycles at room temperature on treatment with a moderately electrophilic palladating agent:[117]



HL^{40} **40** (97%)

Thus, it is clear that cyclopalladation of monodentate phosphines is stimulated by the increase in the size of the P-substituents (*e.g.*, in the series Me < Ph < Bu^t).

It is likely that the activation of the aliphatic C–H bonds can be promoted by an increase in the number of substituents at the carbon atom adjacent to the metallation site. Using platinum analogues as examples, it was found that cyclometallation is markedly accelerated with an increase in the number of β-methyl groups in the $CH_2CR^1R^2Me$ alkyl substituent at phosphorus. Indeed, n-propylphosphine HL^{41} does not form a phosphametallacycle; cycloplatination of isobutylphosphine HL^{42} proceeds only on heating; and neopentylphosphine HL^{43} forms dimer **43′** over a period of several minutes at room temperature.[118, 119] The cyclopalladated derivative **42** is known only for phosphine HL^{42} (see Ref. 119).



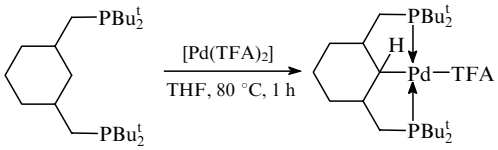
HL^{41}–HL^{43} **42**, **42′**, **43′**

M = Pt: $R^1 = R^2 = H$ (HL^{41}); R^1 = Me, R^2 = H (HL^{42}, **42′**);
$R^1 = R^2$ = Me (HL^{43}, **43′**); M = Pd: R^1 = Me, R^2 = H (**42**).

It is assumed that easier cyclometallation of sterically overcrowded ligands is determined by both the entropy and conformation effects [118, 119] (see Section II.3.a).

It may seem unexpected at first glance that steric stimulation of cyclopalladation of diphosphine ligands by bulky P-substituents is not always observed, the effect being appreciably dependent on the hybridisation of carbon in the C–H bond subject to metallation and perhaps also on the conformational features of the ligand.

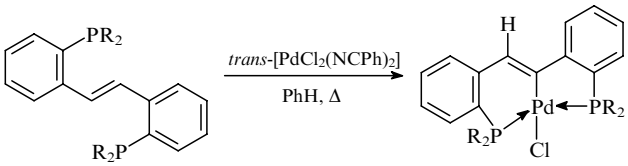
As an example of normal steric promotion, one can mention successful cyclopalladation at the $C(sp^3)-H$ bond of diphosphine HL^{44}, containing PBu^t_2 donor groups. When $Pd(TFA)_2$ is used as the metallating agent, the reaction is completed over a short period and gives the product in a nearly quantitative yield.[91]



HL^{44} **44** (91%)

Recall that a similar ligand, HL^{26}, with PPh_2 donor groups forms only the *cis*-$[Pd(\kappa^2\text{-}HL^{26})(TFA)_2]$ (**26**) coordination complex under the same conditions.[92]

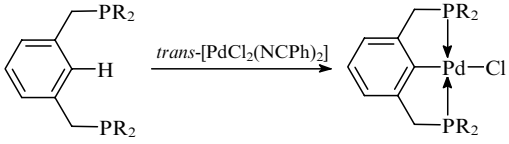
Conversely, in the activation of $C(sp^2)-H$ bonds, an increase in the steric demands of the P-substituents not only does not promote, but hampers this process. For example, cyclopalladation is substantially retarded when the Ph_2P groups in diphosphine HL^{10} are replaced by more bulky $(o\text{-Tol})_2P$ groups to form the HL^{45} ligand [for PPh_3 and $PPh(o\text{-Tol})_2$, the θ values are 145 and 178°, respectively]. The conversion of HL^{10} and HL^{45} into cyclopalladated complexes **10a** and **45a** in comparable yields required heating for 1 and 16 h, respectively.[60, 61]



HL^{10}, HL^{45} **10a** (72%), **45a** (62%)

R = Ph (HL^{10}, **10a**), *o*-Tol (HL^{45}, **45a**).

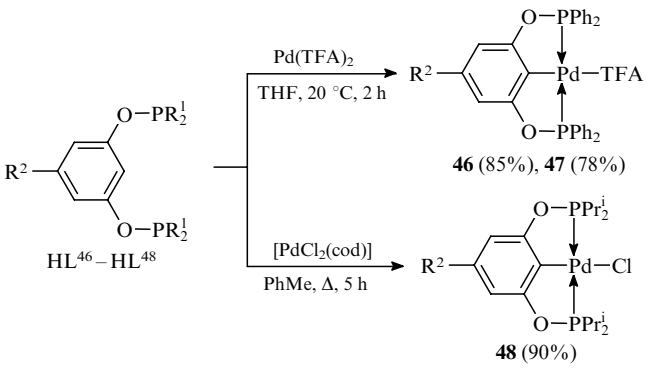
The transformation of steric stimulation into steric impediment is even more obvious from comparison of the metallation conditions of two *m*-xylylene-α,α′-diphosphines HL^{17} and HL^{25}. The HL^{25} ligand with PBu^t_2 groups reacts at much higher temperature and in a more basic solvent (MET, 130 °C, 25 min)[90] than the PPh_2-analogue HL^{17} (CH_2Cl_2, 20 °C, 10 min),[66] despite the much greater cone angles of the P-donor fragments in the former compound (for the monophosphines $BnPBu^t_2$ and $BnPPh_2$, the θ values are 176 and 152°, respectively). The reasons why Milstein and coworkers[120] used much more rigorous conditions (MET, 150 °C) to prepare complex **17a** remain obscure (the yield of the complex is not documented). Presumably, the ease of cyclometallation in these systems is mainly determined by the geometry of the coordination precursors of the *trans*-$[PdCl_2(\kappa^2\text{-}HL)]$ type, in particular, by the degree of proximity of the C–H bond to be activated to the metal.[66]



HL^{17}, HL^{25} **17a** (75%), **25a** (75%)

R = Ph (HL^{17}, **17a**), Bu^t (HL^{25}, **25a**).

The activation of the C–H bond in bis(phosphinites) HL^{46} and HL^{47} based on resorcinols containing the PPh_2 donor groups does not require steric stimulation either: on treatment with palladium(II) trifluoroacetate at 20 °C, PCP-complexes **46** and **47** are formed rather fast (2 h) and in high yields (78%–85%).[121]

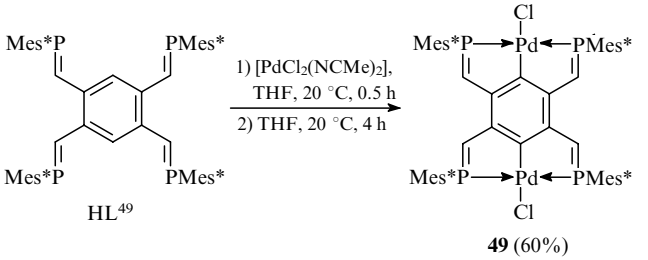


R^1 = Ph: R^2 = H (HL[46], **46**), Me (HL[47], **47**);

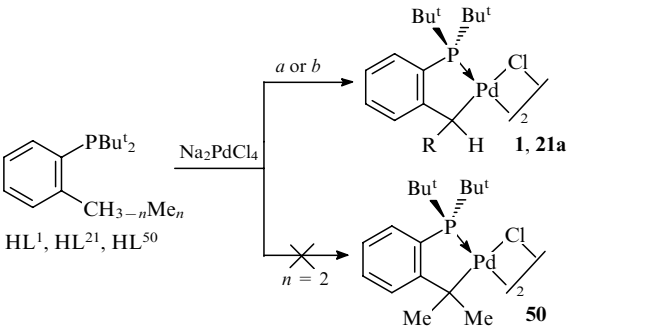
R^1 = Pr^i, R^2 = H (HL[48], **48**); cod is cycloocta-1,5-diene.

Conversely, cyclopalladation of sterically more hindered bis(phosphinite) ligand HL[48] with Pr^i_2P donor groups (for the phosphinites $PhOPPh_2$ and $PhOPPr^i_2$, the θ angles are 139 and 149 °, respectively) is obviously hampered and requires more drastic conditions: high yields in the reaction of HL[48] with $[PdCl_2(cod)]$ were attained after refluxing in toluene for 5 h.[122] This difference in the behaviours of bidentate ligands with PPh_2 and Pr^i_2P donor groups becomes even more significant if one takes into account the fact that the palladating agents used should tend[123] (or do tend[124]) to form mononuclear coordination intermediates (see Section II.3.a).

Apparently, the optimal structure of the coordination precursor makes a certain contribution (apart from the steric assistance from bulky supermesityl P-substituents) to the easy cyclopalladation of bis-*m*-diphosphaethene ligand HL[49] (see Ref. 117) and a number of related substrates.[125–127]



Whereas bulky substituents at the phosphorus atom or in the side chain promote activation of the C–H bonds in monophosphines, the substituents at the carbon atom subjected to metallation appreciably hamper this process.[55,81] This can be illustrated by the conditions of synthesis of PC-palladacycles from (*o*-alkylphenyl)di(*tert*-butyl)phosphines on treatment with Na_2PdCl_4 in alcohols.



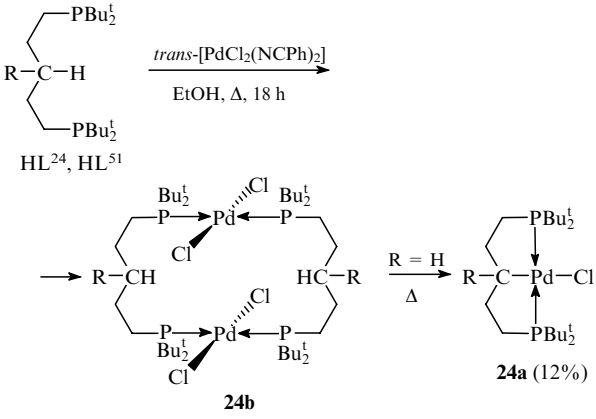
n = 0, R = H (HL[21], **21a**, 90%); n = 1, R = Me (HL[1], **1**, 95%);

n = 2 (HL[50], **50**);

(*a*) ~65 °C, 5 min; (*b*) ~97 °C, 20 min.

The metallation of the secondary C–H bond in the phosphine HL[1] requires a higher temperature and longer time than the metallation of the primary C–H bond in HL[21] analogue, while attempts at activation of the tertiary C–H bond in the phosphine HL[50] have failed at all.[55]

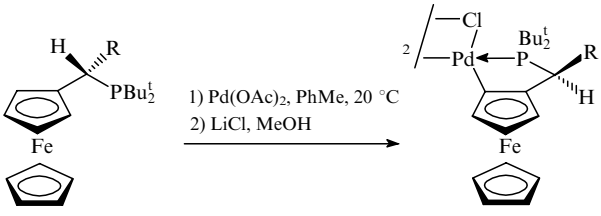
Similar results have also been obtained for reactions of aliphatic diphosphines. For instance, cyclometallation involving the secondary C–H bond in the HL[24] ligand was accomplished in a low yield (12%) by long-term thermolysis of the macrocyclic coordination precursor $[\{PdCl_2(\mu\text{-HL}^{24})\}_2]$ (**24b**) in alcohol;[128] by sublimation of intermediate **24b** *in vacuo* (10^{-2} mm Hg), the yield of the PCP-complex **24a** can be increased to 64%.[89] However, the tertiary C–H bond in the diphosphine HL[51] cannot be metallated under the same conditions.[129]



R = H (HL[24], **24a**,**b**); Me (HL[51]).

It is known from the chemistry of benzylaminate CN-systems that the introduction of any α-substituent (even a small Me group[98,130] and, especially, a bulky group[99–101]) into the side chain near the heterodonor atom promotes appreciably the activation of the aromatic C–H bond. Unfortunately, the possibility of estimating the influence of this factor on the activity of P-donor ligands is limited and the available data are rather contradictory.

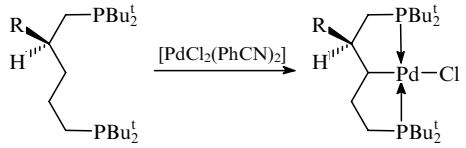
On the one hand, comparison of the reaction conditions and the yields of the products of cyclopalladation of α-ferrocenylalkylphosphines HL[52] and HL[53] with palladium(II) acetate prompts the conclusion that the activation of the aromatic $C(sp^2)$–H bond is accelerated upon the introduction of a substituent into the side chain.[131,132] The reaction with the α-Me-substituted HL[53] ligand proceeds much faster and gives complex **53** in a higher yield (93% in 1 h) than that with the α-unsubstituted analogue **52** (70% in 8 h). Actually, this effect is even stronger, as it is manifested against the background of an additional steric stimulation by the bulky PBu^t_2 donor groups.



R = H (HL[52], **52**), Me (HL[53], **53**).

Signs of same assistance to the activation of the aliphatic $C(sp^3)$–H bond as a result of similar modification of the ligand structure can be found by comparing the cyclopalladation conditions for two aliphatic diphosphines, $Bu^t_2PCH_2CH(R).(CH_2)_3PBu^t_2$ with R = H (HL[24]) and R = Me (HL[54]), on treatment with *trans*-$[PdCl_2(NCPh)_2]$. The PCP-complex derived from the former ligand, **24a**, was isolated in a very low yield (12%) after long-term (18 h) refluxing in ethanol,[128] whereas the synthesis of

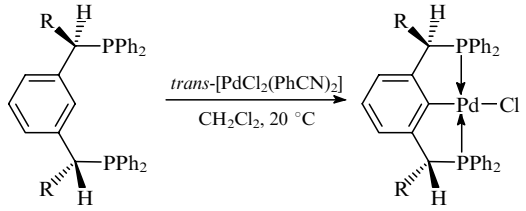
2-methyl-substituted analogue **54** in a moderate yield (36%) required only a 15-minute heating in MET.[133]



HL[24], HL[54] **24a** (12%), **54** (36%)

R = H (HL[24], **24a**), Me (HL[54], **54**).

On the other hand, an adverse influence of α-substituents can be inferred from comparison of reaction durations of *trans*-[$PdCl_2(NCPh)_2$] with the diphosphines HL[17] and HL[55] possessing aromatic core, under identical conditions (CH_2Cl_2, 20 °C) resulting in two related PCP-complexes **17a**[66,134] and **55a**[135]. The palladation of the HL[17] ligand unsubstituted in the benzylic positions required only 10 min, whereas for the cyclopalladation of its α,α′-dimethyl-substituted analogue HL[55], a 24 h period was required.

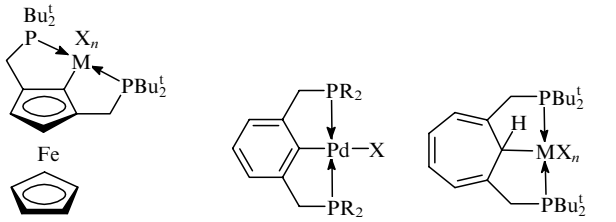


HL[17], HL[55] **17a** (75%), **55a** (85%)

R = H (HL[17], **17a**), Me (HL[55], **55a**).

This anomaly in the behaviour of diphosphine ligands can be due either to the entropy effects [which account for the fact that bulky substituents at phosphorus do not 'work' in these systems (see above)] or to the change in the ligand conformation in the stage of the formation of coordination intermediates. However, it cannot be ruled out that the mechanism of activation of the C—H bonds changes on passing from N- to P-donor ligands, from monodentate to bidentate phosphines, and from $C(sp^3)$—H to $C(sp^2)$—H bonds.

In conclusion, one more parameter important for the cyclopalladation of diphosphines should be mentioned, namely, the P,P-chelate bite angle essential for the formation of the coordination precursor. This parameter is mainly governed by the geometry of the bridging fragment between two P-donor atoms. Apparently, the too large funnel between the side chains in the HL[56] ligand with 1,3-ferrocenedimethylene skeleton (caused by the geometric demands of the five-membered Cp ring) precluded its cyclopalladation to give complex **56** (MX_n = PdCl),[136] whereas analogous 'pincer' complexes of type **A** (for example, **17a**, **25a**, *etc*., see Table 4) with the six-membered *m*-xylylene skeleton are quite accessible.



56′ (MX_n = RhHCl) **A** **57′** (MX_n = IrH(CO)Cl)

However, in this case, some mechanistic restrictions cannot be ruled out, because the formation of the hydride PCP-complex **56′** (MX_n = RhHCl) proved to be possible *via* oxidative addition of the HL[56] ligand to the [{Rh(η²-C_2H_4)$_2$(μ-Cl)}$_2$] dimer.[136] A PCP-complex with a bridge incorporating a seven-membered cycloheptatrienyl ring is unknown for palladium(II), although a similar iridium complex **57′** [MX_n = IrH(CO)Cl] has been obtained by the reaction of HL[57] with iridium(I).[137]

Apparently, the true role of the geometric requirements of five-, six- and seven-membered rings in the bridge connecting two donor phosphorus atoms in diphosphines in the intramolecular palladation giving PCP-structures of types **56**, **A** and **57** would be properly evaluated only after the synthesis (or attempts at the synthesis) of the last representative of this series, complex **57** (M = Pd) using this method.

2. Conditions of direct intramolecular cyclopalladation

From the previous section, it is evident that the ease of activation of the C—H bonds in P-donor ligands largely depends on their structural features. With a specified ligand structure, the success of cyclopalladation is determined to a large extent by the conditions chosen, including the type of the palladating agent and the base, the reactant ratio, the nature of the solvent and the temperature regime. Therefore, two equally important problems are to be solved: ensuring the ligand coordination to palladium through the phosphorus atom(s) and creating conditions for the subsequent intramolecular activation of the C—H bond in the resulting coordination precursor.

a. Standard routes and classical reagents

The set of palladating reagents suitable for the direct activation of the C—H bonds in phosphines, phosphites and phosphinites is rather broad (see Tables 1, 4). It includes simple salts ($PdCl_2$), carboxylates [$Pd(OAc)_2$ and $Pd(TFA)_2$] and palladium(II) complexes: anionic ($[PdHal_4]^{2-}$), neutral {$[PdCl_2(Q)_2]$, where Q = MeCN, PhCN or (Q_2) = cod} and cationic ($[Pd(NCMe)_4]^{2+}$) ones. However, the relative efficiency of the reagents is often not correlated with the efficiency characteristic of the reactions of substrates with more rigid donor atoms.[21]

The activity of the palladating agent depends on the nature of the anionic and neutral ligands bound to the metal and on the charge on the metal atom.

1. The electron density on the metal centre determines its electrophilic or nucleophilic behaviour.

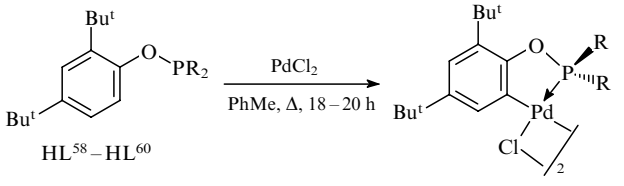
2. The dissociative lability of the ligands bound to the metal is important for the creation of the coordination vacancy.

3. The nature of the ligands bound to Pd controls the steric effects in the coordination sphere.

Depending on the reagent used, both the structure of the coordination precursor formed in the first stage and the reaction route as a whole may vary (see Section II.3.a).

The solubility of the palladating agent in organic media is also important for practical use.

The simplest and the most readily available reagent, the insoluble $\{PdCl_2\}_n$ polymer, is applied rather rarely but in some cases, this reagent works quite satisfactorily. Thus in the *ortho*-palladation of the phosphinites HL[58] and HL[59], the yields of dimers **58** and **59** are 50%—52%, irrespective of the electronic properties of the substituents at the phosphorus atoms (aromatic or aliphatic ones),[138] and an increase in the substituent bulk (for example, for R = 2,4-Bu$^t_2$$C_6H_3O$) results in a nearly quantitative yield of the PC-complex **60**.[139]



HL[58]—HL[60] **58** (52%), **59** (50%), **60** (96%)

R = Ph (HL[58], **58**), Pr^i (HL[59], **59**), 2,4-Bu$^t_2$$C_6H_3O$ (HL[60], **60**).

The $\{PdCl_2\}_n$ reagent is also able to activate the aliphatic C—H bonds provided that an additional steric stimulation is

involved. In the cyclopalladation of trimesitylphosphine HL^{35} on treatment with $PdCl_2$, good yields (70% – 80%) are attained even at 20 °C, although the process is much slower (8 – 10 h) than that with the soluble $[PdCl_2(NCPh)_2]$ complex (0.5 h).[110] Most likely, the lower activity of palladium chloride is due to retardation of the preliminary P-coordination of the ligand under heterogeneous conditions. Nevertheless, the excellent P-donor properties of the ligands (*e.g.*, HL^{58} – HL^{60}) ensure cleavage of the chloride bridges in the polymeric palladating reagent, while their rich hydrocarbon framing allows performing the reactions in nonpolar solvents (toluene, dichloromethane).

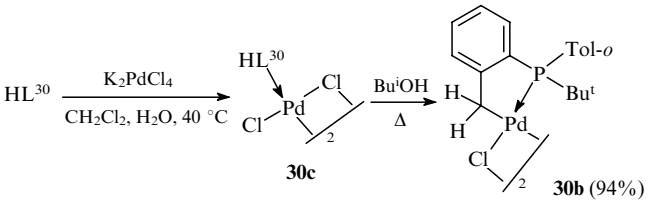
It should be noted that palladium(II) chloride is sometimes used to convert mononuclear bis(phosphine) intermediates into more reactive binuclear complexes in experiments carried out in three stages.[56, 140 – 142]

$$HL \longrightarrow [PdCl_2(\kappa^1\text{-}HL)_2] \longrightarrow \textit{trans}\text{-}[\{PdCl(\kappa^1\text{-}HL)(\mu\text{-}Cl)\}_2] \longrightarrow [\{Pd(\eta^2\text{-}L)(\mu\text{-}Cl)\}_2].$$

The differences caused by the nature of the donor atom are illustrated by the fact that tetrachloropalladates, which are relatively inert in cyclopalladation of N-donor ligands,[21] often ensure almost quantitative yields of the cyclopalladated complexes of the PC-type (mainly, when steric stimulation is involved). Most often, Na_2PdCl_4 is used, and the reaction is carried out in alcohols (MeOH, EtOH, Pr^nOH or MET). In some cases, the stages of monodentate P-coordination and C – H bond activation are carried out separately. Under these conditions, cyclopalladation involving the Me groups of bulky *o*-tolylphosphines ensures good yields of five-membered PC-palladacycles (76% – 97%,[55, 81] see Table 1); they decrease to 60% when the reagent is generated *in situ*.[57] The efficiency of Na_2PdCl_4 is lower in reactions with less bulky ligands ($Bu^iPBu^t_2$,[119] $PhPBu^t_2$,[84] the yields are 40% – 43%) and in the case of activation of aromatic C – H bonds both in phosphines (for $BnPBu^t_2$, the yield is 49%,[82] while for less bulky Bn_2PBu^t, the yield is 13%[82]) and in triaryl phosphites $P(OAr)_3$ (yields 40% – 64%).[143, 144] The decrease in the yields might be partly due to the use of the metal : ligand ratio of 1 : 2; in this case, thermolysis of the coordination precursor in high-boiling solvents is required (MET or decalin).

The drawbacks of sodium tetrachloropalladate include its amorphous structure, which brings about some problems in its purification, while the satisfactory solubility in alcohols is an advantage of this reagent. Strange as it may seem, the lithium salt Li_2PdCl_4, readily soluble in alcohols, which is the most popular reagent (despite its hygroscopicity) in the cyclopalladation of N-donor ligands,[21] has not yet been used for the synthesis of PC-palladacycles.

The crystalline potassium tetrachloropalladate is free from this drawback, however, it is virtually insoluble in alcohols, which has markedly restricted, until recently, the use of this reagent in cyclopalladation. Only one example of the use of K_2PdCl_4 is its reaction with PBu^t_3, which had to be performed in DMF (yield 72%).[69, 70] However, this problem can be solved successfully by passing to a two-phase system at the stage of formation of the coordination intermediate, because potassium tetrachloropalladate is perfectly soluble in water. This approach is illustrated by cyclopalladation of the phosphine $PBu^t(Tol\text{-}o)_2$ (HL^{30}), which includes *in situ* generation of the binuclear coordination precursor **30c** in the $CH_2Cl_2 - H_2O$ two-phase system.[145]

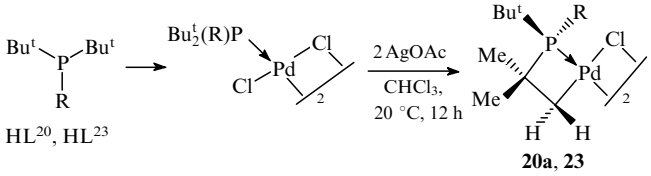


Note for comparison that cyclopalladation of *tert*-butyldi(*o*-tolyl)phosphine by Na_2PdCl_4 in alcohols (see Table 1) afforded dimer **30b** in 84% – 97% yields.[81]

For the formation of PCP-structures, tetrachloropalladates are not used at all and the examples of using the corresponding bromides (K_2PdBr_4) and iodides (Na_2PdI_4) are very scarce (see below).[60, 61]

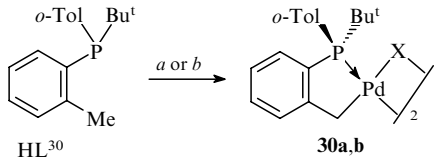
The activation of the $C(sp^3) - H$ bonds in monodentate P-donor substrates is often performed by palladium(II) acetate, which has a macrocyclic trinuclear structure.[146] However, in this case, too, the outcome depends appreciably on the steric demands of the ligand. With thermal promotion of the process (50 – 60 °C), excellent yields of cyclopalladated complexes (> 90%) can be obtained in the reactions of bulky di-*o*-tolylphosphines $(o\text{-}Tol)_2PR$ with R = *o*-Tol, Bu^t (θ = 194 and 190°, respectively) proceeding in 3 – 5 min.[10, 147, 148] Moreover, the reaction can also be carried out at 20 °C; in this case, its duration has to be increased to 6 – 12 h. The yields are correlated with the steric demands of P-substituents, varying from ~40% in the reactions with $P(Tol\text{-}o)Cy_2$ or $P(Tol\text{-}o)_2Cy$ (θ = 178 and 186°, respectively) to 80% – 90% for $P(Tol\text{-}o)Bu^t_2$ or $PMes_3$ (θ = 186 and 212°, respectively).[10]

The cyclopalladation involving aliphatic fragments proceeds more easily when the chloride ligands in the intermediate coordination complexes are replaced by acetate anions on treatment with silver acetate. This method was used to obtain dimeric PC-complexes **20a** and **23** with strained four-membered phosphapalladacycles from the phosphines PBu^t_2R under mild conditions (20 °C). The yields of cyclopalladated complexes increased with increasing steric stimulation of the process from 55% for R = Ph (θ = 170°) to 100% for R = Bu^t (θ = 182°).[84]



R = Bu^t (HL^{20}, **20a**), Ph (HL^{23}, **23**).

However, in the reactions with monodentate phosphines, palladium(II) acetate does not always show noticeable advantages over halides. Reagents of both classes are equally suitable for sterically hindered substrates, for example, for the *o*-tolylphosphines HL^{21} and HL^{30} (see Refs 10 and 81).



X = OAc (**a**), Cl (**b**); (*a*) $Pd(OAc)_2$, PhMe, 60 °C, 5 min, 90%; (*b*) Na_2PdCl_4, Pr^nOH – MeOH, 3 min, Δ, 96%.

Strange as it may seem, until recently, the electrophilic palladium(II) acetate has been seldom used to activate the aromatic $C(sp^2) - H$ bonds in monodentate phosphines. The rare examples of successful use of this reagent refer to cyclopalladation of the bulky α-ferrocenylalkylphosphines HL^{52} and HL^{53} (in yields ranging from 70% to 93%).[132, 149] In the absence of steric promotion, this reagent is of low utility: *ortho*-palladation of the benzylphosphine $PBnPh_2$ (HL^{36}, θ = 152°) in MeOH with heating (60 °C, 3 h) gave the PC-dimer $[\{Pd(\eta^2\text{-}L^{36})(\mu\text{-}OAc)\}_2]$ (**36b**) in a yield of only 19%.[114] A higher yield (85%) was attained in the reaction with more bulky PBn_2Ph ligand (θ = 158°), but this required longer heating (50 °C, 16 h).[150]

Palladium(II) acetate has not yet been used in reactions with diphosphines, although the more electrophilic trifluoroacetate is often used to create PCP-structures. The latter reagent activates

fairly efficiently both aliphatic [62, 91] and aromatic [151, 152] C–H bonds, thus ensuring the yields of cyclopalladated compounds ranging from 75% to 100%; however, in this case, thermal activation is required (70–130 °C). An exception is provided by the bis(phosphinites) HL[46] and HL[47], which react with $Pd(TFA)_2$ at 20 °C without steric promotion giving rise to PCP-complexes in 78%–85% yields over a period of 2 h.[121]

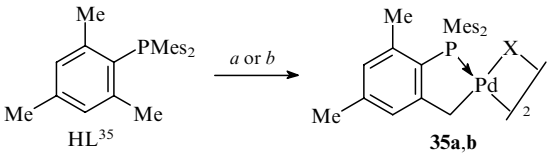
The next group of reagents is comprised by neutral mononuclear palladium(II) complexes with auxiliary ligands. The coordination compounds like *trans*-$[PdCl_2(NCR)_2]$ (R = Ph, Me) are most popular; the benzonitrile complex is known as the Karash reagent.[153] Reagents of this type are convenient from the practical standpoint, as they are readily soluble in organic solvents, both in alcohols or tetrahydrofuran and hydrocarbons (benzene, toluene, dichloromethane). It is more important that nitriles incorporated in these complexes are classified as weakly bound [154] ligands; therefore, they are replaced by P-donor substrates without any difficulty.

Despite the relatively low electrophilicity of the metal centre in the nitrile reagents, they are traditionally used for the synthesis of PCP-complexes (see Table 4); in the activation of the aromatic C–H bonds, they ensure yields of 60%–90% (with rare exceptions [155]). Their efficiency may be illustrated by the fact that some diphosphine and bis(phosphaalkene) ligands can be introduced in the reaction even at 20 °C;[66, 117, 125–127, 134, 135] nearly quantitative yields (75%–90%) of cyclopalladated compounds can be attained in 10–30 min.[66, 126] Nevertheless, in most cases, the activation of the $C(sp^2)$–H bonds is thermally stimulated (80–150 °C).[90, 120, 155, 156] The high efficiency of nitrile reagents with respect to bifunctional substrates with a rigid, aromatic skeleton is due, most likely, to the forced character of cyclometallation caused by the proximity of the C–H bond (subject to activation) to the metal in the coordination precursor if it has the *trans*-P,P-geometry.[66]

Perhaps, this accounts for the lower efficiency of *trans*-$[PdCl_2(NCPh)_2]$ in the activation of aliphatic $C(sp^3)$–H bonds in conformationally flexible diphosphines with a polymethylene bridge.[89, 128, 133, 157] Even upon high-temperature thermolysis (>260 °C) [128] or sublimation *in vacuo*,[89, 157] the yields of cyclopalladated compounds obtained from the pentamethylene-1,5-diphosphines HL[24] and HL[54] do not exceed 40%. However, in the cyclopalladation of the diphosphine HL[27] with the more rigid dibenzyl skeleton by treatment with the same reagent, a high yield of the PCP-complex **27a** (75%) is attained under milder conditions.[60, 61]

Nitrile palladating agents are used somewhat more rarely to prepare monocyclic PC-complexes, although they are rather effective (with rare exceptions [140]) towards the activation of the $C(sp^2)$–H and $C(sp^3)$–H bonds (see Table 1). To attain high yields in the *ortho*-palladation of monodentate benzylphosphines (83%–85%) [113] and phosphites (70%–90%),[56, 138, 141, 142] heating is usually required; however, cyclopalladation of the phosphaalkene HL[40] with the supermesityl substituent proceeds even at 20 °C (the yield of **40** is 97%).[117]

Under equally mild conditions (20 °C, 0.5–2 h), the aliphatic C–H bonds in the bulky phosphines PBu^t_3 and $PMes_3$ are usually activated (the yields are >80% [70, 71] and 98%,[109, 110] respectively). The (benzonitrile)chloride complex competes quite successfully with a powerful metallating agent such as $Pd(OAc)_2$: trimesitylphosphine HL[35] is cyclopalladated by this complex faster and with a higher yield [109] than by $Pd(OAc)_2$ (see Ref. 10).



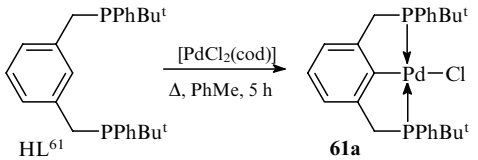
X = OAc (**35a**, 81%), Cl (**35b**, 98%); (*a*) $Pd(OAc)_2$, PhMe, 60 °C, 12 h; (*b*) *trans*-$[PdCl_2(NCPh)_2]$, 20 °C, 30 min.

The efficiency of reagents such as *trans*-$[PdCl_2(NCR)_2]$ is determined, first of all, by the easy replacement of the weakly coordinated nitrile by P- or P,P-donor ligand. Actually, these nitrile complexes can be regarded as solvation-stabilised forms of mononuclear palladium(II) chloride. When the nitrile in these complexes is replaced by a $\eta^2{:}\eta^2$-bound diene in the $[PdCl_2(cod)]$ reagent, restrictions apparently arise already in the stage of ligand coordination to the metal through phosphorus atoms due to both stronger binding of the diene to the metal and steric factors.

For example, all attempts at the intramolecular activation of the $C(sp^3)$–H bond of the trimesitylphosphine HL[35] (θ = 212°) [95] by the diene reagent even under conditions of long-term thermolysis in high-boiling solvents (toluene, xylene) failed, although the use of the benzonitrile reagent furnishes cyclopalladated complex **35a** in a quantitative yield at 20 °C.

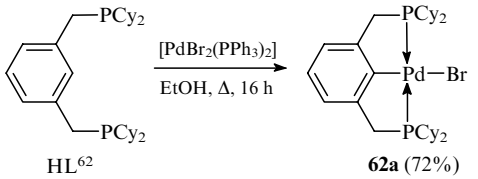
The reason for the lack of success is the fact that the sterically crowded phosphine is unable to displace the diene from the starting $[PdCl_2(cod)]$ complex.[110] The diene reagent is markedly inferior to the benzonitrile analogue also in the reaction with the bulky phosphine PBu^t_3, whose cyclopalladation required 8 days (the yield was not reported),[69] whereas with the use of *trans*-$[PdCl_2(NCPh)_2]$, 70% yield was attained in 2 h.[71]

The activation of aromatic C–H bonds in the bidentate P,P-donor ligands by $[PdCl_2(cod)]$ is somewhat more efficient. Although cyclopalladation of diphosphinite HL[48] with the *meta*-phenylene skeleton [122, 158] and *m*-xylylene-α,α'-diphosphine HL[61] (see Ref. 159) gives PCP-complexes **48** and **61a** in almost quantitative yields (90%–98%), this still requires long-term (5 h) heating in toluene.



Note for comparison that the use of other reagents [the acetonitrile complex [66] or palladium(II) [121] trifluoroacetate] in reactions with related P,P-ligands allows one to attain rather high yields (75%–85%) at 20 °C over short periods of time (10 min to 2 h, see Table 4).

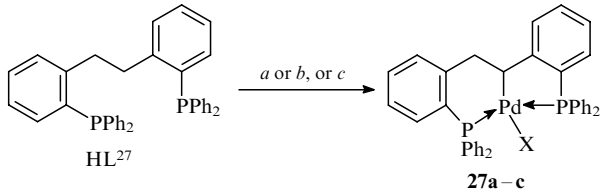
Assuming that the efficiency of nitrile reagents is mainly determined by the ease of replacement of the auxiliary neutral ligand, one should expect that the appearance of phosphines (that are held more tightly by the metal centre) in the palladating reagent would complicate the stage of formation of the coordination intermediate. From this standpoint, the results of cyclopalladation of the HL[62] ligand with a phosphine reagent, *trans*-$[PdBr_2(PPh_3)_2]$, appear rather unexpected: the PCP-complex **62a** has been obtained in a quite satisfactory yield.[155]



Conversely, the reaction of the same HL[62] ligand with the nitrile reagent $[PdCl_2(NCPh)_2]$ gave polymeric coordination complex *trans*,*trans*-$[\{PdCl_2(\mu\text{-HL}^{62})\}_n]$ as the major product; the C–H bond in this complex was activated with moderate success only upon long-term thermolysis (MET, 48 h, yield 31%).[155]

It could be suggested that in the above example, a positive role is played by the replacement of the chloride in the nitrile metallating agent by the bromide in the phosphine analogue. However, this appears unlikely in view of the behaviour of diphosphines with dibenzyl (HL[27]) and stilbene skeletons (HL[10] and HL[45]) with respect to various palladating reagents (see Table 4). For instance, the activation of the aliphatic C–H bond in the diphosphine HL[27]

is obviously hampered upon the replacement of the chloride reagent $[PdCl_2(NCPh)_2]$ by the bromide $K_2[PdBr_4]$ and, the more so, by the iodide $Na_2[PdI_4]$. Under similar conditions, the yield of the PCP-complexes **27** either sharply decreases (X = Cl, 75%; X = Br, 26%), or remains comparable (X = I, 86%) provided that the reaction duration is increased five- to seven-fold.[60,61]



X = Cl (**a**), Br (**b**), I (**c**); (*a*) $[PdCl_2(NCPh)_2]$, MET, Δ, 1.5 h, 75%; (*b*) K_2PdBr_4, MET, Δ, 2 h, 26%; (*c*) $[PdI_2(PPh_3)_2]$, MET, Δ, 10 h, 86%.

Similar effects are also observed in the cyclopalladation of the vinyl fragment in the diphosphines HL[10] and HL[45] with the stilbene skeleton. On passing from $[PdCl_2(NCPh)_2]$ to K_2PdBr_4 and then to $[PdI_2(PPh_3)_2]$, the temperature regime become more drastic and the reaction duration increases; simultaneously, the yield of the cyclopalladated compound decreases (see Table 4).[60,61]

A similar halide-induced effect has been found in a study of *ortho*-metallation of phosphites of the $P(OAr)_3$ type (Ar = Ph, *o*-, *m*-, *p*-Tol, *p*-ClC_6H_4).[143,144] The thermal activation of the $C(sp^2)-H$ bond in the coordination complexes $[Pd(HL)_2Hal_2]$ is substantially hampered upon the variation of the halide in the series Cl < Br < I: under the same conditions (decalin, Δ, 3 h), the yield at this stage decreases 2.5-fold on the replacement of Cl^- by Br^-, and in the case of the iodide analogue, only traces of the PC-palladacycle are formed.

Unfortunately, such comparison has not been carried out for monodentate phosphines, although a process acceleration could be expected upon the replacement of Cl^- by Br^- and then by I^-. This assumption follows from several considerations, which are outlined below.

1. Cycloplatination of phosphines in the $[Pt(HL)_2Hal_2]$ type coordination complexes[86,160] is accelerated in the series Cl < Br < I, whereas for phosphites, the opposite order was found.[144]

2. In the complexation of the phosphine $PPhBu^t_2$ (HL^{23}) with palladium(II), this sequence (Cl < Br < I) reflects the increase in the tendency to form binuclear complexes in which the subsequent cyclopalladation proceeds more easily due to appearance of a coordination vacancy through cleavage of halide bridges. For example, the $[Pd(HL^{23})_2Cl_2]$ complex reacts with LiI being converted into the binuclear intermediate $[\{Pd(HL^{23})I(\mu\text{-}I)\}_2]$.[83]

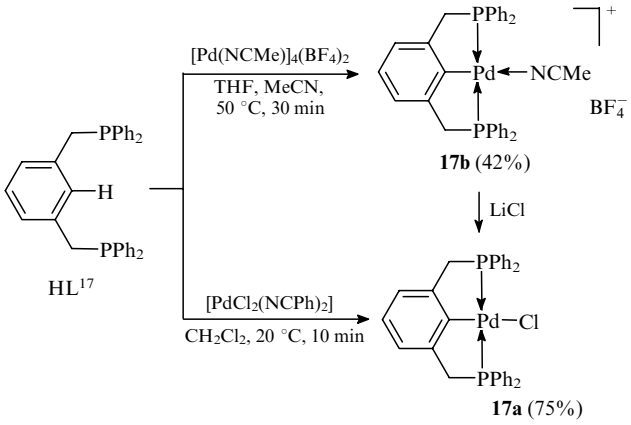
3. The same dependence on the nature of the halide (Cl < Br < I) was observed in the case of intermolecular activation of C–H bonds by $[Pd(PPh_3)_2Hal_2]$ type complexes.[161,162]

Unfortunately, systematic investigations of the role of the anions in the palladating reagents of the similar structure or in the coordination intermediates of the same type are scarce. The true reasons for the halide effects remain obscure; in all probability, the final outcome depends on a complex combination of the electronegativity and the size of the halide atoms, their leaving-group properties and the tendency to accomplish the bridging function. All this is superimposed onto the steric effects stemming from the ligand subjected to metallation. A significant contribution to the slowing of cyclopalladation following the change in the nature of the halide (Cl < Br ≪ I) can be made by the increase in the strength of their binding to the metal (Lewis acid of class *b*).[154]

At first glance, cationic reagents of the $[Pd(NCR)_4]^{2+}$ type[163] free from halides and containing easily dissociating nitrile ligands appear especially attractive. The positive charge of the metal centre should ensure its high electrophilicity in the activation of the aromatic C–H bonds. However, analysis of the available published data shows that the situation is not that unambiguous.

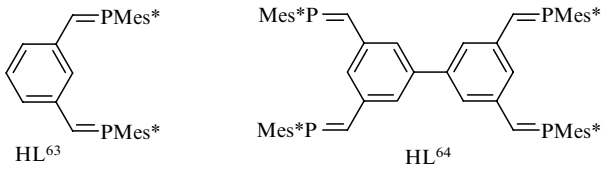
The use of reagents of this class has been limited so far to cyclopalladation of only bidentate substrates with an aromatic skeleton, mainly *m*-xylylene-α,α′-diphosphines and their dendrimer analogues.[48–50,164,165] Most often, the preliminarily obtained $[Pd(NCMe)_4](BF_4)_2$ complex is used;[163,166,167] however, it can be generated *in situ*, for example, by treatment of a suspension of palladium chloride in acetonitrile with a stoichiometric amount of $AgBF_4$ with heating.[49]

The advantages of this approach include the possibility of isolation of the intermediate acetonitrile solvate **17b**, which is especially useful for the subsequent introduction of weakly coordinated ligands. However, most often, this solvate is converted without isolation into standard chloride PCP-complex, for example, **17a**.



Unfortunately, the efficiency of this highly electrophilic cationic reagent is evidently lower than expected (see Table 4). In most cases, the PCP-complexes are isolated in moderate (42%–67%)[48,49,164] or even in low yields (15%–20%);[50,165] in some cases, the reaction does not proceed at 20 °C[48,127,165] and requires refluxing in acetonitrile.[49,50,164] The best results were obtained with generation of the solvated $[Pd(NCMe)_4](BF_4)_2$ reagent *in situ*. In this case, the acetonitrile derivative **17b** was isolated in 90% yield.[49]

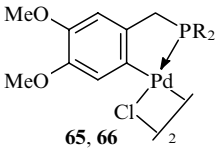
The cationic complex $[Pd(NCMe)_4](BF_4)_2$ is far inferior in activity to the neutral chloride analogue, $[PdCl_2(NCPh)_2]$. The yield of the PCP-complex **17a** is lower with the former reagent[164] than with the latter,[66] despite a longer reaction time and a higher temperature. The same conclusion follows from comparison of the outcome of cyclopalladation of bis(phosphaalkenes) HL[63] (Ref. 125) and H_2L[64] (Ref. 126) (see Table 4). The reason for the lower efficiency of the cationic reagent is not clear, although a possible main reason is reduction of the reagent (extensive isolation of palladium black during the reaction has been noted[165]).



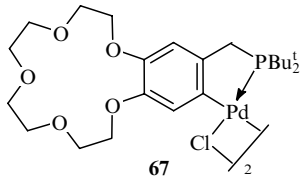
The role of the bases in cyclopalladation of P-donor substrates also differs from that observed for the N-analogues.[21] Phosphines and phosphites have lower basicities than N-donor ligands with a similar structure, but it varies over a fairly broad range depending on the nature of the substituents at the phosphorus atom. According to the pK_a values for the corresponding conjugate acids $[HPR_3]^+$ (see Refs 52–54), the basicity of aliphatic tertiary phosphines $PAlk_3$ is rather high (pK_a 8.0–11.4); but it markedly decreases on passing to triarylphosphines (pK_a 2.7–5.3) and sharply decreases for phosphites (pK_a from −1.8 to −2.0).

Nevertheless, P-donor substrates can often be cyclopalladated without introduction of an additional base. This function can be performed by phosphine ligands themselves; thus the isolation of the corresponding phosphonium salts as the chloride, $[HPBu^t_3]^+Cl^-$,[70] the tetrafluoroborate, $[HPBu^t_2(C_6H_4Et\text{-}2)]^+BPh^-_4$,[55] and the tetrachloropalladate, $[HPBu^t_3]^+_2[PdCl_4]^{2-}$,[69] from the reaction mixture (after cyclopalladation) has been reported.

The necessity of adding a base arises in the case of low-reactivity ligands. Usually, sodium acetate is used as the base; triethylamine[82] or potassium carbonate[140] are less effective and are used less often. Examples of substantial acceleration of the process following the introduction of a proton acceptor are few and mainly refer to reactions of benzylphosphines. Thus the metallation of PBu^t_2Bn (HL^{22}) on treatment with $[PdCl_4]^{2-}$ in boiling MET in the presence of AcONa proceeds much faster (0.5 h, 75%) than without a base (5 days, 64%).[82] *ortho*-Palladation of a less bulky substrate, PBu^tBn_2 (HL^{37}), was accomplished (in a yield of only 12%) only upon the addition of AcONa.[82] The base effect is most pronounced in the case of dialkoxy-substituted benzylphosphines; the C–H-bond activation in the HL^{65} and HL^{66} ligands under the action of *trans*-$[PdCl_2(NCPh)_2]$ is totally impossible without a base, and that in the case of HL^{67} occurs only by 10%. The same reactions carried out in the presence of AcONa in boiling MET ensure high yields of *ortho*-palladated dimers **65** and **66** (81%–84%), the reaction time (2 and 0.5 h) being dependent on the degree of steric assistance from the P-substituents (θ = 152 and 176°, respectively).[113]



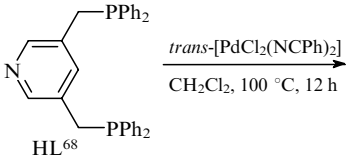
65, **66**



67

R = Ph (**65**), Bu^t (**66**).

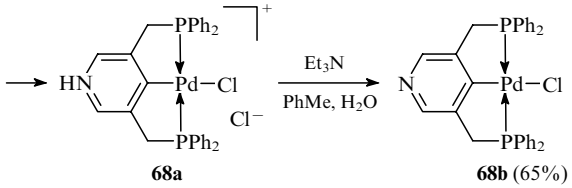
In the cyclopalladation of the diphosphine HL^{68} with the lutidine skeleton, the pyridine ring of the ligand serves itself as the acceptor of liberated protons; hence, the reaction yields first the ionic PCP-complex **68a**, which is converted into neutral compound **68b** under the action of a base.[168]



HL^{68}

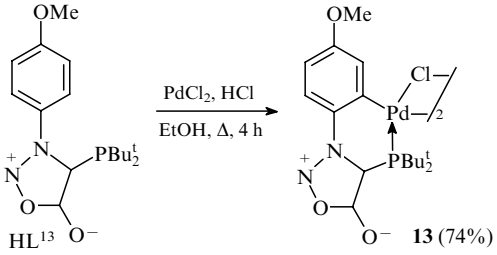
trans-$[PdCl_2(NCPh)_2]$

CH_2Cl_2, 100 °C, 12 h



68a **68b** (65%)

However, under certain conditions, a base does not facilitate cyclometallation and, moreover, it can even inhibit the process. In addition to the known acid-catalysed cyclopalladation of $HPMes_2$ (see Section II.2.b),[169] noteworthy is the activation of the C(sp^2)–H bond in (3-arylsydnonyl)phosphine HL^{13}, which takes place in acid medium (EtOH, conc. HCl), to give the unfavourable six-membered PC-metallacycle in dimer **13**.[63]



HL^{13} **13** (74%)

The possibility of stimulating the cyclopalladation by changing the nature of the solvent has not been studied in systematic mode; the choice of the medium was dictated first of all by the structure of the palladating reagent and the desire to conduct the reaction under homogeneous conditions. It can be suggested from general considerations that highly solvating polar and protic solvents should be favourable for the creation of a coordination vacancy. Perhaps, it is for this reason that alcohols (a MeOH–EtOH mixture,[81] Pr^nOH,[55] Bu^iOH,[145] MET[82,119]) are used for the transformation of chloride coordination precursors into cyclopalladated complexes using alcohols .

When choosing the solvent, one should take into account its ability to compete with the substrate for the site at the metallic centre. Thus cyclopalladation of the secondary phosphine $HPMes_2$ proceeds faster in THF or CH_2Cl_2 than in acetone and becomes impossible in a readily coordinating solvent, acetonitrile.[169] Apparently, for the same reason, cyclopalladation of tri(*tert*-butyl)phosphine under the action of potassium tetrachloropalladate in DMF requires 12 h, whereas the reaction of the same phosphine with $[PdCl_2(NCPh)_2]$ in CH_2Cl_2 is over after 2 h under the same conditions (20 °C, reactant ratio 2 : 1).[70]

The reactant ratio in cyclopalladation is among the most important factors determining the reaction rate, most of all, in 'halide' routes. The metal-to-ligand ratio influences the efficiency of vacation of the coordination site needed for the activation of the C–H bond. This goal is difficult to attain for Pd : HL = 1 : 2 due to the strong binding to the metal of all ligands in the bis(phosphine) intermediate of the $[Pd(HL)_2Hal_2]$ type. Therefore, it comes as no surprise that reactions with this stoichiometry often require rather drastic conditions (up to refluxing in decalin),[143,144] while the yields of cyclopalladated compounds leave much to be desired[82,143,144] (see Table 1). In addition, under these conditions, the reactions often do not give the dimeric complex, but instead, result in its adduct with the starting P-donor ligand.[69,143,144,170]

When equimolar amounts of reactants are used, the problem of generation of a coordination vacancy can be easily solved due to the cleavage of the halide bridges in the binuclear intermediate of the $[\{PdHal(HL)(\mu\text{-}Hal)\}_2]$ type, which allows this reaction to be carried out under milder conditions with good product yields.[57,81]

The reactant ratio becomes almost insignificant only when the process is efficiently sterically stimulated, for example, in reactions of phosphines such as PBu^t_3,[70,71] $PMes_3$,[109,110] and $P(Tol\text{-}o)_2Bu^t$.[81]

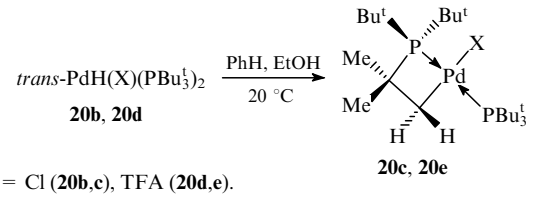
b. Organometallic reagents in cyclopalladation

A special group of cyclometallation processes is comprised by reactions involving organometallic or hydride reagents or intermediates. As a rule, these synthetic protocols show clear advantages over the classical methods considered above, possibly, due to different in kind mechanisms of transformations.

The C–H bonds of monodentate phosphines can be activated within hydride intermediates, $[PdH(X)(HL)_2]$. This approach has been mainly developed using di- and tri(*tert*-butyl)phosphine ligands as substrates.[71,171] The standard route to these hydrides[71,172,173] includes oxidative addition of the acid HX to a palladium(0) complex with the corresponding phosphine, $[Pd^0(HL)_2]$;[174] the existing alternative ways are based on the reduction of Pd(II) bis(phosphine) complexes, for example, by sodium borohydride.[175] The method including a short-term (0.5 h) heating of $PdCl_2$ with PBu^t_3 in DMF at 115 °C is more efficient and practically convenient (the yield of the hydride complex is 90%).[73]

Although hydride complexes of this type are rather stable in the solid state, in solutions, their phosphine ligands are cyclometallated rather easily (at 20 °C).[73] This process depends appreciably on the solvent and on the nature of the anion. In

dichloromethane, the reaction proceeds more rapidly than in benzene and it is markedly accelerated upon the addition of alcohol.[71, 171] The effect of the anion nature is clear-cut and differs from that observed for classical reagents (see Section II.2.a). For example, the hydrido chloride complex **20b** is converted into the phosphine adduct **20c** six times as fast (0.5 h) as the trifluoroacetate analogue **20d** (2 – 3 h), and the hydrido bromide precursor provides instantaneously the phosphapalladacycle, which is formed as the dimer **20a** (apparently, for steric reasons) rather than its mononuclear phosphine derivative.[71, 171]



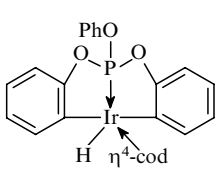
X = Cl (**20b**,**c**), TFA (**20d**,**e**).

Cyclometallation of mono- and dihydride platinum phosphine complexes proceeds equally easily and obeys the same type of dependence on the nature of the anion.[176] The [PdH(Cl)(AsBu$^t_3$)$_2$] hydride with bulky arsine ligands also readily forms a palladacycle (as an unusual dimeric compound with two hydride bridges),[177] whereas the standard coordination complexes cannot be involved in this process.[178]

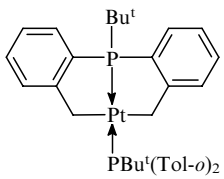
The high efficiency of hydride complexes can be illustrated by closure of an additional four-membered palladacycle due to intramolecular activation of the C – H bonds of the PBu^t group in the iridium(III) PCP-complex [(η^3-HL′)IrH(Cl)] (H_2L' is the 4-MeO-substituted analogue of the HL[25] ligand), resulting in the formation of the [5.5.4]-tricyclic PCPC-complex, [(η^4-L′)Ir(Cl)].[32] No transformations of this type have been described in the chemistry of pincer palladium complexes, although their hydride derivatives are known.

The electronic state of the metal in the coordination precursors changes crucially following the appearance of C-bound ligands, which can serve as efficient acceptors for the proton liberated during cyclometallation or participate in the reductive elimination together with the hydride ligand formed upon the oxidative addition of the phosphine C – H bond. An alternative interpretation of the role of these ligands is easy generation of a vacant coordination position due to protolysis of the Pd – C bond.

The high activity of intermediates with M – Me bonds is well known. One can mention *ortho*-metallation of triphenylphosphine in the [MeRh(PPh$_3$)$_3$] complex, resulting in a strained four-membered PC-metallacycle and liberation of methane,[179] and double *ortho*-metallation of the simple phosphite P(OPh)$_3$ (H_2L^{69}) through the coordination intermediate [MeIr(cod)(H_2L^{69})], which furnishes bicyclic CPC-structure **69′**.[31]



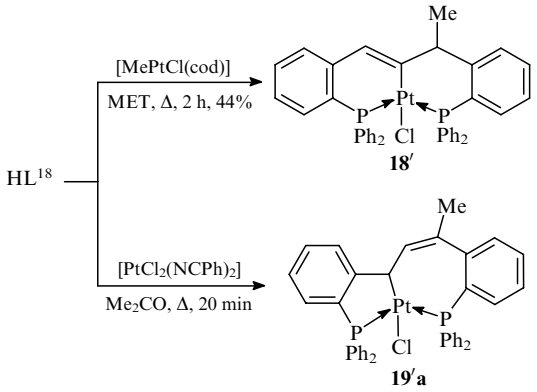
69′



30′

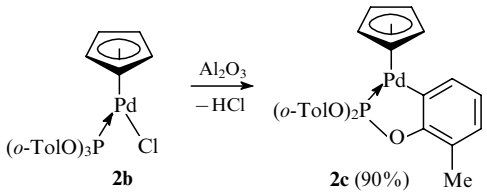
The efficiency of replacement of halides by Me groups in the coordination intermediates of the [M(HL)$_2$X$_2$] type (X = Cl, Me) has been demonstrated with platinum(II) compounds.[115] The activity of organometallic intermediates can be illustrated by the formation of the [Pt(η^2-L)$_2$] bis(chelate) complexes from phosphine adducts of the [MePt(η^2-L)(κ^1-HL)] type [HL = PBu^t_n.(Tol-*o*)$_{3-n}$, where *n* = 1, 2] due to the activation of the C – H bond in the monodentatate phosphine ligand [30, 180] and by double cyclometallation of PBu^t(Tol-*o*)$_2$ at both *o*-tolyl fragments, giving rise to the CPC-structure **30′**.[30] Unfortunately, transformations of this type have not been studied for palladium analogues; palladium spiro complexes are available only through *ortho*-lithiated ligands (see Section IV), while the palladium(II) CPC-complexes are still unknown. This difference between the reactivities of compounds of the two d^8 metals might serve as indirect evidence pointing to different mechanisms of C – H bond activation.

The passage from classical to organometallic reagents can result in switching to another metallation site due to the modification of the reaction mechanism. Two different platinacycles obtained from the same HL[18] ligand can serve as examples.[68]



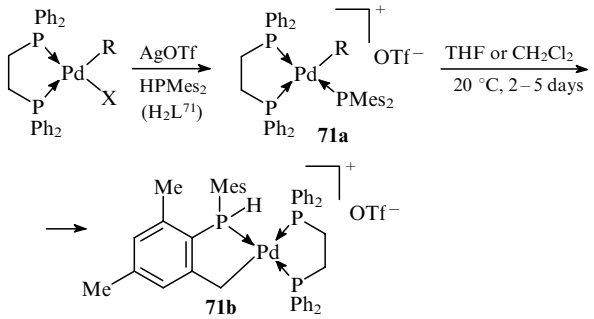
Although no comparison of the behaviours of the two types of reagent in the cyclopalladation of the HL[18] ligand has been carried out, it can still be suggested that this approach can be useful not only for facilitating the process but also for modification of the reaction pathways in systems that contain several alternative reaction sites.

One can only regret that organometallic reagents are seldom used for cyclopalladation. One of the few examples is easy activation of the C(sp^2) – H bond in the phosphite HL[2] in the [Pd(η^5-Cp){P(OTol-*o*)$_3$}Cl] complex, which takes place under unusual conditions — during chromatography of this compound on neutral alumina.[57] The regularities typical of classical systems (see Section II.2.a) are retained; these include the 'halide' effect (the iodide analogue of **2b** is inactive)[57] and the preferred formation of the five-membered PC-metallacycle {a four-membered ring is not formed from the [Pd(η^5-Cp)(PBu$^t_2$Ph)Cl] complex}.[84]



As yet another example of C – H bond activation with participation of a support, one can mention the quantitative formation of the cyclopalladated compound [{(η^2-L[70])Pd(μ-Cl)}$_2$] (**70**) on passage of the [{(κ^1-HL[70])PdCl(μ-Cl)}$_2$] coordination complex with the AsMes$_3$ ligand (HL[70]) through silica gel. The effect appears even more impressive in view of the fact that cyclopalladation of the HL[70] ligand could not be accomplished by the reaction with [PdCl$_2$(NCPh)$_2$] even in boiling benzene.[109]

An absolutely different role is played by the aryl or alkyl groups (Ph, Me) attached to palladium in the cyclometallation of the secondary dimesitylphosphine HPMes$_2$ (H_2L^{71}). The monodentate P-coordination of this bulky ligand giving cationic intermediates of the [(dppe)PdR(κ^1-H_2L^{71})]OTf (**71a**) type [dppe is 1,2-bis(diphenylphosphino)ethane, OTf is trifluoromethanesulfonate] is possible only after the removal of the halide ion from the reagent. A C(sp^3) – H bond of one of the *o*-Me groups of the mesityl substituent is activated on long-term keeping of solutions of these coordination precursors in CH_2Cl_2 or THF at 20 °C to give cationic complex **71b**.[169]



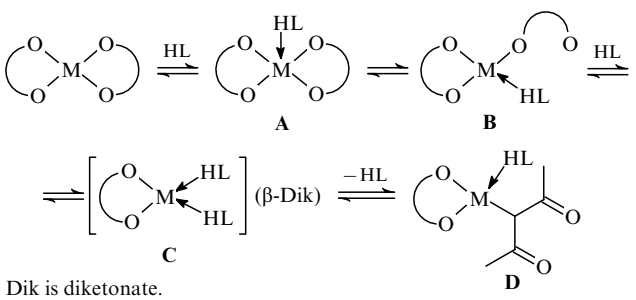
R = Me, Ph.

High activity of the intermediates containing alkyl or aryl groups bound to the metal is indicated by the fact that cyclopalladation of the secondary phosphine H_2L^{71} could not be accomplished using Pd(II) acetate. Detailed studies of the reactions of $HPMes_2$ with palladium(II) showed that cyclopalladation is catalysed by acids (presumably present as impurities in the solvents or reactants used) and inhibited by bases. Protolysis of the Pd–R bond needed for generation of the coordinatively unsaturated 14-electron species $\{(dppe)Pd^{II}(H_2L^{71})\}$ was confirmed by identification of the corresponding hydrocarbons RH (by spectroscopy and using ^{13}C-labelled model compounds). However, the researchers cited do not rule out the possibility of alternative pathways including oxidative addition of the P–H bond or benzyl C–H bond to palladium(II) followed by the reductive elimination of the hydrocarbon RH.[169]

Cases of acid catalysis (through organometallic intermediates) are also known in cycloplatination chemistry. Thus only in the presence of catalytic amounts of HCl, does the phosphine PPr^i_3 (HL^{72}) in the intermediate $[MePt(\kappa^1\text{-}HL^{72})_2(OTf)]$ complex form a four-membered metallacycle.[181]

The selectivity of the $PHMes_2$ (H_2L^{71}) → **71a** → **71b** transformation is remarkable due to the presence of two other potential reaction sites in the ligand molecule: activation can involve both the P–H bond of the secondary dimesitylphosphine H_2L^{71} (*via* deprotonation or oxidative addition) and the P–C(Mes) bond (processes of the latter type are known in the chemistry of arylphosphine complexes of transition metals [182]). It is noteworthy that both reaction directions are realised for the phosphine H_2L^{71} on the platinum(0) centre, giving rise to the phosphide complexes, [(dppe)PtH($PMes_2$)] and [(dppe)Pt(Mes)(PHMes)], respectively.[183]

Interesting possibilities appear when palladium(II) bis(β-diketonate) complexes are used as palladating agents. The synthetic routes to reagents of this class are simple and well-known,[184] and their complexation with N-[185–189] and P-donor ligands [185–187,190–194] have been the subject of detailed research for many years. The set of transformations of β-diketonates on palladium centres caused by the introduction of the additional ligand is fairly diverse.[195] On the basis of kinetic studies,[188,192] it was suggested that the reaction gives first five-coordinate species **A** with O,O′-chelated β-dicarbonyl ligands, one of which then partly undergoes dechelation (**B**). With excess Lewis base (HL), the β-diketonate ligand can be displaced from the metal coordination sphere (**C**) and returns there again after the rerarrangement

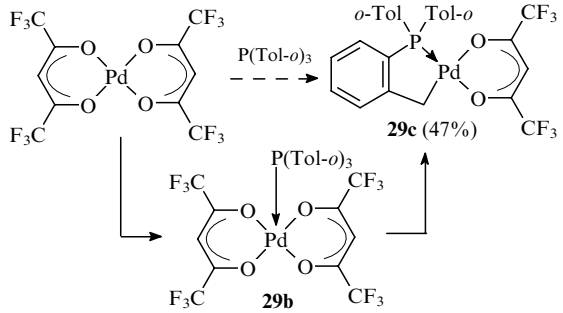


Dik is diketonate.

into the γ-C-bound state (**D**). The structures of the species involved in these multistage processes have been convincingly confirmed by both spectroscopic methods (*in situ* or after isolation) and X-ray diffraction, for example, for five-coordinate adducts of the $[Pd(hfac)_2(PR_3)]$ type ($hfac^-$ is hexafluoroacetylacetonate; R = *o*-Tol [191,196] or Ph [197]).

As regards the use of β-diketonate complexes for cyclometallation, species of type **A** and **D** seem to be the most valuable. In the former type of species, the monodentate O-coordinated β-diketonate with the hard donor atom is weakly bound to the metal and can easily depart, thus leaving a free coordination site needed for the activation of the C–H bond. In organometallic species of type **D**, the γ-C-bound diacylmethyl group $(RCO)_2CH^-$ can not only serve as a good acceptor for the protons being liberated but should also decrease substantially the electron density at the metallic centre due to conjugation and thus enhance its electrophilic properties. In this respect, the hexafluoroacetylacetonate reagent should be more reactive than the acetylacetonate analogue.

The efficiency of the β-diketonate reagents in the cyclometallation was first demonstrated for the *ortho*-palladation of primary benzylamine,[189,198] which had long been considered to be absolutely impossible.[21] Unfortunately, the use of this approach for the cyclopalladation of phosphines is limited to two examples,[116,196] and only one of these studies gives quantitative data.[196] The activation of the C–H bond in tri(*o*-tolyl)phosphine on treatment with palladium(II) bis(hexafluoroacetylacetonate) occurs with moderate success (the yield is 47%), but the reaction proceeds under mild conditions (20 °C), the transformation of the intermediate five-coordinate $[Pd(hfac)_2P(o\text{-}Tol)_3]$ (**29b**) adduct into the cyclopalladated compound **29c** being possible even in the solid phase during long-term storage of the sample.[196]

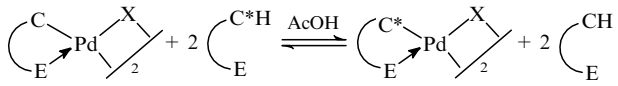


A certain role in this process may be performed by steric promotion: the large bulk of the phosphine ligand (θ = 194°)[95] hinders the rotation about the P→Pd bond in the five-coordinate precursor **29b**, which is manifested as non-equivalence of the three *o*-methyl groups in the ^1H NMR spectra recorded at −55 °C (δ 1.72, 2.10 and 2.94 ppm).[196] The substantial dispersion of these signals ($\Delta\delta$ > 2.2 ppm) may be related to the effect of the paramagnetic anisotropy of the metal on the protons of one of these groups located in the apical position near palladium. Thus, the stereochemistry of the coordination intermediate is favourable for the activation of the phosphine C–H bond.

Mention should be made of the synthetic pathway provided by the use of more readily available cyclopalladated complexes as metallating agents. This is the exchange of cyclopalladated ligands (ECL).[199,200] Recently,[201,202] the term 'transcyclometallation' has been proposed for these reactions.§ Detailed investigations of this process for N-donor ligands [99,200,203,204] have shown that it is

§ Although this concise term may seem attractive, it is not quite adequate to the process in question, because a similar term, 'transmetallation' is used to describe the processes based on replacement of one metal by another (rather than one ligand by another). Perhaps, it would be more appropriate to introduce the term 'transligandation' of palladacycles, which would describe the exchange of ligands at the same metallic centre.

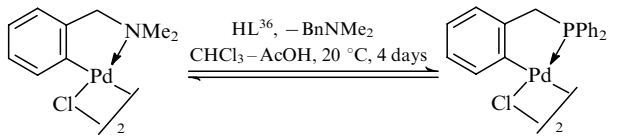
fairly efficient with respect to 'difficult' N-donor substrates and can be useful for the preparation of palladacycles that are inaccessible or accessible with difficulty by other, simpler methods. In the simplified form, the ECL can be represented as follows:



E is the heterodonor atom.

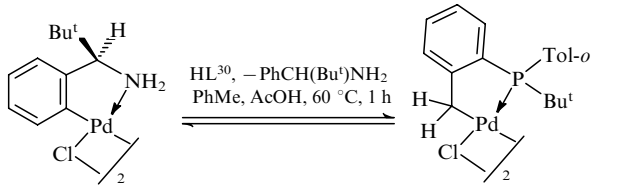
The views on the mechanism of the exchange of cyclopalladated ligands are rather contradictory. Both a dissociative route, which implies the destruction of the initial palladacycle as far as to the closure of a new ring,[199,200] and an associative route with a bis(chelate) intermediate containing both the initial and the new palladacycles have been considered.[203] Irrespective of the views on the mechanism, reactions of this type are carried out in protic media, most often, in acetic acid or its mixtures with aprotic organic solvents.

One can only regret that the use of this approach to phosphapalladacycles is limited to single examples. The use of the simplest CN-palladacycle (**A**) based on *N,N*-dimethylbenzylamine for the activation of the aromatic C–H bond of diphenylbenzylphosphine (HL^{36}) has been reported.[205] However, the cyclopalladated CN-complex proved to be inefficient in this process, like simpler but highly electrophilic $Pd(OAc)_2$. The dimer **36a** has been obtained in a yield of only 21%,[205] while its μ-acetate analogue (**36b**), in 19% yield.[114]



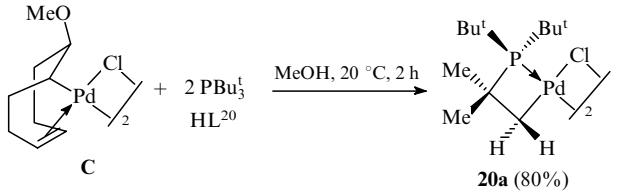
A **36a** (21%)

Some progress along this line has been attained due to the structural modification of the CN-reagent. When the cyclopalladated derivative of primary benzylamine (**B**) was introduced in the reaction with the phosphine $P(o\text{-Tol})_2Bu^t$ (HL^{30}) in the presence of acetic acid with heating, the dimer **30b** was obtained in 71% yield.[206,207]



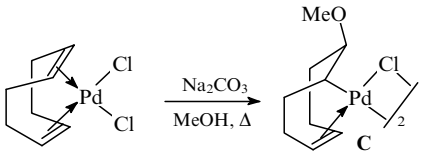
B (R_P,S_P)-**30b** (71%)

Formally, cyclopalladation of the tri-*tert*-butylphosphine HL^{20} under the action of the organometallic dimer **C** should be attributed to the same type of processes.[74] This reagent can be regarded as a specific analogue of a cyclopalladated complex in which the double bond of the alkene fragment replaces the heterodonor centre.



C **20a** (80%)

Unfortunately, this reaction is not discussed by the authors, but the data presented in the Experimental clearly indicate that it smoothly proceeds under mild conditions to give dimer **20a** in a high yield. The type **C** reagents are quite accessible through methoxypalladation[208] of the metal-bound cycloocta-1,5-diene in the commercially available $[PdCl_2(cod)]$ complex, which can also be generated *in situ*.[209,210]



C

The data considered in this Section demonstrate that organometallic reagents possess high (and in some cases, unusual) activities in cyclopalladation. Although this field has not been adequately explored as yet, further progress along this line can provide valuable results.

3. Mechanistic aspects of the direct intramolecular cyclopalladation of P-donor ligands

Two features distinguish the cyclopalladation processes of P-donor ligands from those of substrates with harder donor atoms: first, the pronounced steric effects and, second, high stability of the intermediate coordination compounds. The latter feature is exceptionally convenient from a practical standpoint, because the problem of oxidative instability of phosphine ligands is eliminated when they are coordinated through heteroatom(s). In addition, even this preliminary stage largely determines the possibility (and ease) of the subsequent activation of the C–H bond. Therefore, analysis of the structural peculiarities of coordination precursors deserves attention, first of all, as a way of estimating the true causes of steric promotion of cyclopalladation processes.

a. Coordination intermediates

Usually, three factors are considered as underlying the steric effects involved in cyclopalladation: the entropy (a substantial portion of the inner rotation entropy is lost even in coordination precursors), enthalpy (the number of unfavourable interactions decreases upon cyclisation) and conformational factors (the conformational mobility of the ligand coordinated through the heteroatom decreases or the ligand is fixed in a rotamer that ensures proximity of the C–H bond suitable for activation with the metallic centre).[68,96,97,118,119] With fairly high steric crowding of the phosphine ligands, the barriers to rotation around the P→Pd and P–C bonds in the coordination complexes may increase, so that the rotamers can be detected by spectroscopy,[55,81,180,211–214] in some cases, even at 20 °C.

For the coordination intermediate to be perfectly prepared for the subsequent proper cyclometallation step, its structure should ensure not only the proximate positions of the C–H bond to be activated and the metal, but also the possibility of formation of a free coordination site in the equatorial plane. Presumably, effective solution of the last-mentioned problem in sterically overcrowded systems makes a substantial contribution to the steric assistance to the C–H bond activation.

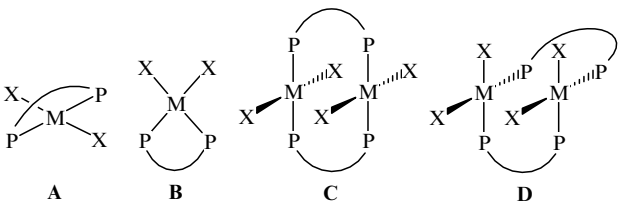
The reactions of monodentate P-donor ligands with halide-containing palladating agents are often (especially in early publications) carried out in two or even in three stages with isolation of intermediate mono- or binuclear complexes of the $[Pd(\kappa^1\text{-}HL)_2Hal_2]$ or $[\{Pd(\kappa^1\text{-}HL)Hal(\mu\text{-}Hal)\}_2]$ type depending on the reactant ratio. The problem of formation of a coordination vacancy in these precursors can be solved in several ways. In complexes with bulky P-donor ligands, the P→Pd bonds are weakened,[215] which have to facilitate the phosphine dissociation. Indeed, a partial dissociation of *tert*-butyldi(*o*-tolyl)phosphine (HL^{30}) from the intermediate coordination complex, $[Pd(\kappa^1\text{-}HL^{30})_2Cl_2]$, was confirmed by molecular mass measurements (508 against the calculated value of 718).[81] In palladium(0) phosphine complexes, the coordination number of the metal decreases from four to two following an increase in the steric requirements of the ligands,[174,215–218] irrespective of their basicities.[216]

It is also assumed [97] that bulky ligands can stabilise coordinatively unsaturated species resulting from elimination of one of the ligands through steric shielding of the vacant site. A certain stabilising role can also be played by secondary interactions with the metal.[174, 217] Under these conditions, the structure of the initial intermediate (mono- or binuclear) is virtually insignificant. Apparently, this is why cyclometallation of sterically crowded ligands depends only slightly on the reaction conditions (see Section II.1).

In addition, due to the large number of unfavourable interactions between bulky substituents of the phosphine and *cis*-arranged ligands (usually halides) in bis(phosphine) complexes, they tend to be transformed into binuclear halide-bridged compounds [55, 219] (they are formed even at a metal : ligand ratio of 1 : 2 [55]). These binuclear complexes readily dissociate owing to cleavage of the halide bridges to give coordinatively unsaturated species. The tendency for the monomer → dimer transformation is known to increase with an increase in the size of the halide ion or its ability to perform the bridging function in the sequence $Cl^- < Br^- < I^-$. Thus upon the replacement of the chloride in *trans*-$[Pd(PPhBu^t_2)_2Cl_2]$ by iodide, the binuclear $[\{PdI(PPhBu^t_2)(\mu\text{-}I)\}_2]$ complex is formed instead of the expected mononuclear analogue, *trans*-$[Pd(PPhBu^t_2)_2I_2]$.[83] However, the dependence of the ease of cyclometallation on the nature of the halide follows the opposite order, indicating the predominant role of other factors at subsequent stages.

In the absence of steric promotion, the advantage of binuclear coordination precursors for the subsequent cyclopalladation becomes more pronounced. This can be confirmed by the results of a study of the H/D-exchange in mono- and binuclear complexes, $[Pd(HL)_2Cl_2]$ and $[\{Pd(HL)Cl(\mu\text{-}Cl)\}_2]$ [HL = (*o*-Tol)P(Ph)Hex (HL[33]) and (*o*-Tol)P(Me)CH_2CH_2Tol-*o* (HL[34])].[108] Only for binuclear compounds, was the H/D-exchange detected for the *o*-methyl group of the P-tolyl substituent upon prolonged storage of the compounds as solutions in d_4-methanol at 20 °C, which was indicative of reversible C–H bond activation. Although the corresponding phosphapalladacycles have not been synthesised (due to insufficient steric stimulation), their formation was detected in mass spectroscopic studies of the same binuclear coordination precursors. However, in the case of mononuclear bis(phosphine) intermediates, no activation of the C–H bond was observed.[108]

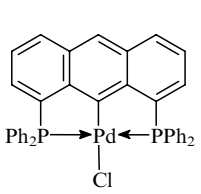
The structure of the coordination intermediates is also important for the cyclopalladation of diphosphine ligands. Unfortunately, purposeful studies of such intermediate complexes are scanty. The types of coordination of diphosphines are diverse and include both mononuclear structures with a P,P-chelating ligand with either *trans*- (**A**) or *cis*-geometry (**B**) and binuclear complexes with a bridging P,P-ligand linking two metal centres in either *trans*- (**C**) or *cis*-configuration (**D**).[123] The formation of coordination polymers cannot be ruled out either.



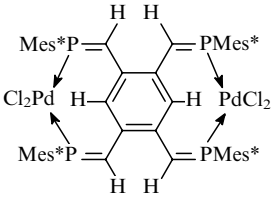
A **B** **C** **D**

It is reasonable to suggest that the optimal geometry of the coordination precursor should be largely determined by the structure of the fragment connecting two P-donor atoms. In the general case, *trans*-P,P-chelation is preferred for the subsequent cyclopalladation. This geometry ensures the closest proximity of the metal and the C–H bond to be activated, which is located in the middle of the bridging fragment in the vast majority of known ligands. However, the structure of such coordination intermediates has been convincingly confirmed only in a few cases.

In the coordination of a diphosphine having a rigid anthracene-1,8-diyl skeleton (HL[73]), the central C–H bond and Pd are forced to approach each other. The interaction of the ligand with the metal cannot be limited to only *trans*-P,P-chelation (despite the quite acceptable distance between the two phosphorus donor atoms equal to 5 Å) due to steric hindrance created by the C(9)–H bond of the anthracene skeleton; therefore, the formal insertion of the metal into this bond to give PCP-complex **73** becomes inevitable.[156]



73



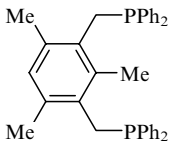
49b

The forced character of proximity of the metal atom and the C–H bond to be activated in the coordination precursor **49b** (detected by spectroscopy) was suggested for cyclopalladation of the H_2L[49] ligand.[117] This spatial proximity can be partly responsible (together with steric assistance of bulky supermesityl P-substituents) for the subsequent exceptionally easy cyclometallation of this and other similar ligands [125–127] (see Table 4).

The necessity of a mononuclear *trans*-chelate structure for the coordination intermediate of type **A** has also been assumed for cyclopalladation of diphosphines with relatively rigid *m*-xylylene skeletons.[66, 67, 155] However, no data on the isolation or reliable spectroscopic identification of such complexes have been reported as yet.

The possibility of controlling the types of ligand pre-coordination appears fairly attractive; however, studies of this type are scarce.[123, 155] For example, a study of cyclopalladation of *m*-xylylene-α,α′-diphosphine HL[62] by $[PdCl_2(PhCN)_2]$ has revealed predominant formation of an inactive polymeric coordination complex, *trans*,*trans*-$[\{PdCl_2(\mu\text{-}HL^{62})\}_n]$, whereas with the use of the phosphine-containing reagent $[PdBr_2(PPh_3)_2]$, cyclopalladation proceeds rather smoothly. While discussing the role of the phosphine ligand in the $[PdBr_2(PPh_3)_2]$ reagent, the researchers suggest that it can catalyse the rearrangement of the polymeric coordination intermediate into a mononuclear species with the *trans*-P,P-geometry, needed to bring together the C–H bond to be activated and the metal.[155]

A more detailed study [123] of the influence of neutral ligands in palladating agents on the structure of the coordination intermediates has been carried out using complexation with the diphosphine HL[74] as the example.



HL[74]

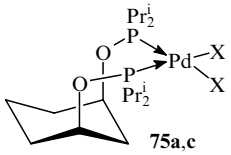
The cyclopalladated derivative of this diphosphine is unknown; however, the synthesis of its analogues **11** and **12** with two six-membered metal rings has been reported.[62]

The requirements of the structure of an optimal coordination precursor can vary depending on the position of the C–H bond subject to activation relative to the metal. This is the case on passing from *m*-xylylenediphosphine HL[17] to its homologue HL[74]. In the researchers' opinion,[123] of the three possible structural types of coordination complexes **B**–**D** (mononuclear *trans*-structures of type **A** are not considered in this work), the closest position of the specified $C(sp^3)$–H bond to the metal can be ensured only in the mononuclear species **B** having the *cis*-P,P-geometry.

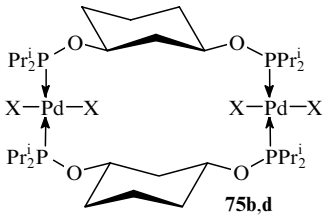
An important result of this study is the established relationship between the type of coordination and the nature of the palladating reagent. Thus the reaction of the HL[74] ligand with

the nitrile reagents $[MCl_2(NCR)_2]$ (M = Pd, Pt; R = Ph, Me) at 20 °C gives selectively and quantitatively only binuclear macrocyclic compounds of the *trans*, *trans*-configuration with a bridging diphosphine (type **C**). The structure of the complex *trans*,*trans*-$[\{PdCl_2(\mu\text{-}HL^{74})\}_2]$ was confirmed by X-ray diffraction. However, the complexation of HL^{74} with the diene reagent $[PtCl_2(cod)]$ gives, equally selectively, the mononuclear complex *cis*-$[PtCl_2(\kappa^2\text{-}HL^{74})]$ with P,P-chelating diphosphine of type **B** with an eight-membered ring.[123] Although the reasons for these differences remained unknown, the possibility of controlling the process at the stage of coordination precursors is undoubtedly useful. For the subsequent cyclometallation, which is often carried out at elevated temperatures, it is also important that the binuclear platinum(II) complex of type **C** is converted into thermally more stable mononuclear compound of type **B** under relatively drastic conditions (CH_2Cl_2, 140 °C, autoclave).[123]

Possibly, type **A** or **B** mononuclear complexes are also formed intermediately in the reactions with palladium(II) trifluoroacetate. First, using this reagent, cyclopalladated derivatives of the PCP-type (complexes **11** and **12**) have been prepared from diphosphines similar to the ligand HL^{74} but containing PBu^t_2 and PPr^i_2 donor groups.[62] Second, mononuclear complex **75a** with the *cis*-P,P-configuration (type **B**) was the major product (72%) in the reaction of $Pd(TFA)_2$ with bis(phosphinite) HL^{75}, whereas the binuclear macrocyclic compound **75b** with the *trans*,*trans*-geometry is only a minor product under these conditions (8%). The structures of both coordination complexes isolated as iodides **75c** and **75d** were confirmed by X-ray diffraction.[124]



75a,c

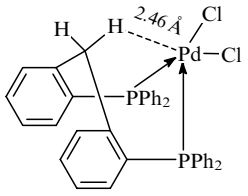


75b,d

X = TFA (**75a**,**b**), I (**75c**,**d**).

Probably, the efficiency of palladium(II) trifluoroacetate in the cyclopalladation of P,P-donor ligands is due, among other factors, to its tendency towards the formation of mononuclear (rather than binuclear or polymeric) coordination intermediates. An unsuccessful attempt at cyclopalladation of the bis(phosphinite) HL^{75} through the precursor **75a** with the *cis*-P,P-geometry [124] suggests that the activation of the C(sp^3)—H bond in ligands of this type should be preceded by a rearrangement of the mononuclear coordination intermediate from the *cis*-P,P- into the *trans*-P,P-configuration, which is hampered due to conformational features of the cyclohexane fragment. Indeed, the structural parameters of the complex **75a** clearly show that the *endo*-hydrogen of the central methylene group is removed away from the metal by a distance (CH···Pd = 3.725 Å),¶ longer than the sum of the van der Waals radii of these atoms (3.1 Å [220,221]). The activation of this C—H bond would require an essential structural reorganisation.

However, even when the structure of the coordination precursor appears optimal, this still does not guarantee the success of the subsequent activation of the C—H bond. The unsuccessful attempt to cyclopalladate the diphosphine HL^{28} can serve as an example of such restrictions. Even long-term (3 h) refluxing of this diphosphine with $[PdCl_2(NCPh)_2]$ gives only the coordination complex *cis*-$[PdCl_2(\kappa^2\text{-}HL^{28})]$ (**28**), despite the potential possibility of the formation of two optimal five-membered phosphapalladacycles.[94]



28

This seems even more surprising in view of the fact that an X-ray diffraction study of the coordination precursor **28** showed the occurrence of a close contact between the *endo*-hydrogen atom of the methylene group of the diphosphine and the metal (the distance is 2.46 Å). The substantial downfield shift of the ^{1}H NMR signal of this proton with respect to the signal of the *exo*-proton ($\Delta\delta$ = 2.7 ppm) confirms that the boat conformation is retained in solutions. Thus, the close geometric proximity of the metal and the C—H bond potentially suitable for activation is a necessary but not a sufficient condition.

The formation of mononuclear complexes with a *trans*-P,P-chelated ligand (type **A**) seems to be more realistic in the case of diphosphines with a flexible and rather long polymethylene bridge. The structure of these complexes has been the subject of keen attention at an early stage of research into their cyclometallation.[222–224]

It is believed that the preferableness of *trans*-P,P-chelation for long-chain diphosphines at the stage of coordination intermediates is determined by the presence of bulky PBu^t_2 groups (as opposed to the PPh_2 analogues, which usually form linear polynuclear species at this stage). The bulky donor groups restrict the freedom of rotation not only about the P→Pd and P—C bonds but also about the C(α)—C(β) and C(β)—C(γ) bonds of the polymethylene bridge, thus predetermining its conformation.[96,128,222–224] This type of pre-coordination should result in localisation of one of the central methylene groups in the axial position above the metal, thus ensuring the necessary proximity of one C—H bond with the metal. However, the coordination complex of type **A** — *trans*-P,P-$[Pd(HL^{76})Cl_2]$ — was isolated only upon the reaction with the decamethylenediphosphine $Bu^t_2P(CH_2)_{10}PBu^t_2$ (HL^{76}), whereas in the case of its pentamethylene analogue, HL^{24}, no signs of formation of mononuclear species were detected.[224] The most typical coordination complexes formed by these ligands are bimetallic macrocycles with the bridging diphosphine (type **C**).[128,129,222,224] The structures of *trans*, *trans*-$[\{Pd(\mu\text{-}HL)Cl_2\}_2]$ complexes with pentamethylenediphosphines HL^{24} (see Ref. 128) and HL^{44} (see Ref. 129) were confirmed by X-ray diffraction.

To conclude this Section, we can make some assumptions concerning the causes for the difference between the behaviours of mono- and diphosphines in cyclopalladation (see Section II.1). Most likely, the difference between them is due to entropy effects. Whereas the formation of a PC-palladacycle from the coordination intermediate with a monodentate phosphine is usually accompanied by a substantial decrease in the system entropy, in the case of diphosphines, the entropy has markedly decreased already upon their bridging P,P-coordination and, even more so, in the case of P,P-chelation.

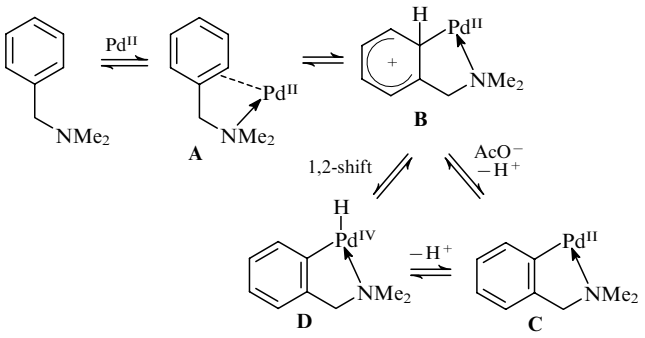
b. The stage of activation of the C—H bonds

The importance of the processes of the C—H bond activation involving transition metal complexes (especially, in the catalytic regime [225–227]) dictates the permanent interest in experimental [80,162,228] and theoretical [229–234] studies in this field. However, most of the known relevant reviews consider intermolecular processes.[80,226,235,236] Only a few studies deal with analysis of the specific features of the intramolecular activation of C—H bonds by various transition metals,[14,237–241] and only some of these studies touch upon the mechanisms of reactions involving palladium.[238–240] Some general views on the mechanisms of

¶ Data from the Cambridge Structural Database; code MEXRID.

intramolecular activation of C—H bonds can be found in reviews on cyclometallation.[15, 17, 19]

It is generally believed that the activation of aromatic C—H bonds occurs *via* preliminary η^2-coordination of the arene fragment to the metal, which allows the reaction to follow a lower-energy pathway.[14, 80, 240] This accounts for the apparent anomaly: many metals are capable of even intermolecular activation of strong aromatic C—H bonds ($\sim$110 kcal mol^{-1}), but for weaker aliphatic C—H bonds (96– 102 kcal mol^{-1}), this process is impossible or substantially hampered.[80] A similar mechanism has been assumed for cyclopalladation.[240]



The intramolecular activation of the C(sp^2)—H bond in dimethylbenzylamine includes the preliminary η^2-coordination of the metal to the aromatic ring of the N-bound ligand and subsequent transformation of intermediate **A** into arenonium species **B**. In the classical versions of electrophilic cyclometallation,[14, 238] the process of formation of metallacycle **C** from **B** ends with proton elimination under the action of a base. However, the possibility of a 1,2-shift of hydrogen from the *ipso*-carbon atom of the arenonium species **B** to the metal with the intermediate formation of a Pd(IV)-containing hydride derivative of metallacycle **D** also cannot be ruled out.[240]

This version of the reaction seems even more likely if one recalls that Pd(IV) complexes[242–245] have ceased to be exotic compounds during the last decade. An extensive series of organometallic Pd(IV) derivatives has been prepared, including compounds with phosphine ligands[246, 247] and structures with CC-[248] and CN-palladacycles.[249] In the presence of stabilising ligands, Pd(IV) compounds become rather stable and can be isolated;[248–252] some of these are stable in solutions even at elevated temperatures.[240] The structures of most of these complexes were confirmed by X-ray diffraction.[248, 249, 251, 252]

η^2-Arene complexes which model intermediate **A** are also known, many of them have been studied not only by spectroscopy but also by X-ray diffraction.[253–257] Detailed analysis of their structural parameters[256] resulted in the suggestion that the mode of coordination of the arene fragment to palladium should rather be interpreted as being intermediate between η^2- and η^1-modes,[258] because the *ipso*-carbon of the arene ring is the main donor of π-electron density. In addition, in a recent study, direct transformation of such complexes into CC-palladacycles has been observed.[259, 260]

In most of the generally accepted mechanistic schemes proposed for cyclopalladation, an essential role is assigned to agostic interactions between the metal and the C—H bonds to be activated, both aliphatic[261, 262] and aromatic[263, 264] ones. It is believed that the oxidative addition of alkanes is preceded by η^1-, η^2- or η^3-coordination of the CH_n fragments to the metal.[235] The ease of this process depends on the degree of substitution of the carbon atom to be metallated both from purely statistical considerations ($CH_3 > CH_2 \gg CH$) and for steric reasons, because the access of the metal to the C—H bond becomes more complicated with an increase in the number of substituents in its surroundings.[241] An argument in favour of the possibility of subsequent oxidative addition of the aliphatic C—H bond to the palladium centre is provided by spectral identification of the hydrido(alkyl) [PdH(Cy)Br$_2$(PPh$_3$)$_2$] species in the intermolecular activation of cyclohexane by the [PdBr$_2$(PPh$_3$)$_2$] complex.[162]

Contacts of the Pd$\cdots$H type were detected by crystallography in many palladium compounds with bulky phosphines.[174, 217, 265, 266] For instance, in the structure of *trans*-[PdI$_2$(PMe$_2$Ph)$_2$], the Pd$\cdots$H distance between the Pd atom and the *o*-hydrogen atom of the benzene ring (in the axial position) is shortened to $\sim$2.8 Å (see Ref. 265). The substantial downfield shift of the ^{1}H NMR signal for the *o*-protons ($\delta > 9$ ppm) indicates that these axial contacts are also retained in solution.[174, 217] However, the direction of this shift is opposite to that expected of true agostic interactions, which impart a hydride nature to the hydrogen atom.

It has been assumed that the interaction of Pd with the C—H bond located in the axial position (even at distances shortened to 2.1 Å) is destabilising, but it can become attractive when the bond shifts to the coordination plane.[237] Therefore, bringing the Pd atom closer to the axial hydrogen atom can be a useful step in the overall process of C—H bond activation. This can be considered as a desirable condition but it does not ensure the success of cyclometallation. For example, the *trans*-[PdI$_2$(PMe$_2$Ph)$_2$] complex mentioned above[265] does not form a four-membered phosphapalladacycle, although the corresponding platinum analogues are known.[85]

Although agostic complexes with a two-electron three-centre C—H$\rightarrow$M bond are regarded as intermediates or transition states in the metallation of aromatic substrates,[267] cases where they have been isolated are rare. Recently,[264] such complexes have been synthesised by the reaction of a cationic Rh(I) reagent with the diphosphine HL^{25} and its 4,5,6-trimethoxy-substituted analogue. The structure of the former product, [Rh(HL^{25})CO]$^+$, was confirmed by X-ray diffraction. Moreover, an increase in the acidity of the aromatic proton involved in the agostic interaction was noted: its ^{1}H NMR signal is shifted to δ 4.13 ppm. The deprotonation of the agostic precursor giving rise to the PCP-complex [Rh(η^3-L^{25})(CO)] is easily induced by the action of weak bases (triethylamine or collidine). This process models the last stage of the electrophilic cyclometallation of diphosphines at the arene fragment. It has been suggested[264] that in this case, the contribution of the pathway involving the classical arenonium intermediate is small, if present at all.

These results are of interest as an illustration of the extensive potential for changing individual steps of the overall mechanism of C—H bond activation by varying not only the structures of the process participants but also the reaction conditions. For example, a decrease in the electron density on the metallic centre of the reagent proved to be sufficient to make Rh(I), known for its nucleophilic properties,[238, 239] react with the highly basic diphosphine HL^{25} by an electrophilic mechanism. Presumably, this pathway could also be realised in intramolecular activation of C—H aromatic bonds by palladium(II), which is more prone to electrophilic behaviour.

Comparative analysis of the available experimental data on the cyclopalladation of P-donor ligands with participation of both aromatic and aliphatic fragments (see Section II.1) has shown that mono- and bidentate ligands behave differently: the activation of aromatic C(sp^2)—H bonds is facilitated only for diphosphines and diphosphites (see Table 4), whereas for monodentate phosphines, it is rather hampered. If the role of the η^2-arene or agostic intermediate is assumed to reduce to bringing the metal closer to the C—H bond being activated, then the difference between mono- and diphosphines can be related to the fact that in the latter case, the tight contact is attained automatically even upon *trans*-P,P-coordination of the ligand, whereas in the case of monodentate ligands, conformational reorganisation is required.

The information on the mechanisms of direct intramolecular activation of C—H bonds in P-donor ligands by palladium is extremely sparse. It can only be suggested from general considerations that the reaction pathway should depend on a number of factors: the nature of the central metal atom and the donor atom

of the ligand [14, 15] (in particular, the ratio of its σ-donor to π-acceptor properties);[51, 53] hybridisation of and the electron density on the carbon atom in the C−H bond being metallated and the steric factors in its surroundings; the possibility of agostic or other secondary interactions between this bond and the metal, or η^2-coordination of the metal to the double bond of the aromatic ring.[14]

Apparently, the electron density on the metallic centre in the intermediate coordination complexes is one of the most important factors, because it determines the metal susceptibility to oxidative addition or to electrophilic attack. The former pathway is typical of electron-enriched metals; for Pd(II), electrophilic behaviour is assumed most often, whereas Pt(II) occupies an intermediate position.[15, 237, 238]

In the absence of experimental data, assumptions concerning the cyclometallation mechanism are often made on the basis of the influence of the nature of the metal on the ease of the process. This criterion is justified by the easier oxidative addition to Pt(II) compared to that to Pd(II) and by the lower stability of Pd(IV) complexes. Indeed, direct activation of the C−H bonds in phosphines and phosphites under the action of Pt(II) compounds often occurs much more easily than that with Pd(II)-containing reagents.[15, 59, 69, 81, 82, 86, 129, 143] However, numerous exceptions to this rule can be found. For example, cycloplatination of bulky ligands such as trimesitylphosphine [110] and *tert*-butyldi(*o*-tolyl)-phosphine [81] proceeds at higher temperatures than cyclopalladation. This points indirectly to the possibility of changing of the process mechanism. Similar anomalies can also be found among reactions of diphosphines. For example, attempts at cycloplatination of *m*-xylylene-α,α′-diphosphine HL[62] have not met with success, while it can be cyclopalladated quite readily by the action of *trans*-[$PdBr_2(PPh_3)_2$].[155] These contradictions can be due to the change in the mechanism of the proper C−H bond activation stage. However, difficulties in the stage of the coordination through heterodonor atoms caused by steric factors [268] or by kinetic intertness of Pt(II), which is several orders of magnitude higher than that of Pd(II), also cannot be ruled out.

The electron density on the metallic centre is largely determined by the nature of the attached organic ligands, in particular, the nucleophilic behaviour becomes more probable on passing from N- to P-donor substrates.[14] This assumption is supported by the increase in the activity of Ni(0) complexes with respect to the oxidative addition following the introduction of phosphines into the Ni(0) coordination sphere and the subsequent increase in the phosphine basicity [241] (for PPh_3 and PEt_3, the pK_a values are 2.73 and 8.69, respectively [53]).

$$[Ni(cod)(bipy)] < [Ni(PPh_3)_4] < [Ni(PEt_3)_4]$$

bipy is 2,2′-bipyridyl.

The increase in the electron density on the metal atom with an increase in the basicity of the coordinated phosphines was convincingly confirmed by calorimetric measurements of the protonation enthalpies of complexes ($-\Delta H_{HM}$). For example, upon replacement of PPh_3 by PMe_3 (pK_a 2.73 and 8.65, respectively), the basicity of complexes increases by 3−7 kcal mol^{-1} (see Ref. 269).

However, in view of the predominant influence of steric effects in the cyclopalladation of P-donor ligands, this criterion should be treated with caution. Indeed, from the standpoint of electronic effects and with the assumption of the electrophilic mechanism, one cannot interpret the failure [82] or the difficulty [114, 205] of the *ortho*-palladation of the benzylphosphine $PhCH_2PPh_2$ against the background of the brilliant results attained in the *ortho*-palladation of more bulky $PhCH_2PBu^t_2$.[82] An idea of the relative basicities of these two ligands can be gained from comparison of this parameter for phosphines PPh_3 and PBu^t_3 (pK_a 2.73 and 11.4, respectively).[53] If we assume that the considerable increase in the basicity of the metallic centre caused by the coordination of trialkylphosphine is responsible for the success of the reaction, this prompts the idea that the reaction has a nucleophilic mechanism. However, this conclusion is faulty, as indicated by the pronounced acceleration of the reaction upon the introduction of MeO substituents into the aromatic ring,[113] which attests in favour of an electrophilic pathway.

The attempts to predict the reaction mechanism on the basis of the effect of substituents in the triarylphosphine cannot be considered legitimate: in addition to the expected influence of substituents in the aromatic ring on the C−H bond being metallated, the electronic effects can be transferred to the metal through the donor phosphorus atom. The introduction of electron-donating substituents increases the electron density in the aromatic ring (and thus increases its susceptibility for the electrophilic attack), but the electron density on the metal also increases and this enhances its tendency for the oxidative addition.[14, 86] For example, the protonation enthalpy of [$Fe(CO)_3(PAr_3)_2$] type complexes (Ar = Ph, *p*-$MeOC_6H_4$) increases from 14.1 to 16.2 kcal mol^{-1} upon the introduction of *p*-MeO substituents into the triphenylphosphine ligand (the pK_a values for these ligands are 2.73 and 4.59, respectively).[269] This transfer of electronic effects makes problematic the choice between alternative mechanisms on the basis of this criterion and for the given class of ligands.

The formal charge of the metal is considerably affected by the anions linked directly to the metal. The measured protonation enthalpies of the complexes with different halides [269] provided a paradoxical outcome: their basicity increases along the sequence $I^- < Br^- < Cl^-$, opposite to that expected on the basis of electronegativities (but consistent with the proton affinity of these anions in the gas phase). A similar conclusion was drawn from detailed X-ray diffraction and ^{13}C, ^{19}F and ^{31}P NMR studies of organometallic complexes of the *trans*-[$(PPh_3)_2Pd(Ph)Hal$] type: the affinity of halides to palladium(II) in nonpolar media increases in the series $I^- < Br^- < Cl^- < F^-$ (see Ref. 270). This 'halide anomaly' is at variance with the standard views on the greater affinity of soft bases (here, I^-) for soft acids such as Pd(II). Presumably, for complexes of the type mentioned above and for other compounds of d^8 metals, this anomaly can be interpreted in terms of the concept of repulsion of filled orbitals (two-orbital four-electron destabilisation).[270] A certain contribution might be made by the change in the ratio of the σ- to π-donor properties of the anions.[269]

From the studies of cycloplatination of the P-donor ligands through the coordination precursors [$Pt(HL)_2X_2$], it is known that in the case of phosphines, the reaction rate decreases depending on the nature of the halide in the series I > Br > Cl,[85, 86] whereas on passing to phosphites, the order of reactivity is reversed (Cl > Br > I).[143, 144] On the basis of these data, it is usually assumed that reactions with phosphines proceed by a nucleophilic mechanism, while those with phosphites follow an electrophilic mechanism.[17]

For coordination complexes of palladium(II) with phosphites [143, 144] and phosphines, similar patterns of dependence of the reaction rate on the nature of the anions are obeyed, namely, Cl > Br > I (see Section II.2.a).

Examples of a similar dependence of the ease of cyclopalladation on the nature of the halide (Cl > Br > I) can also be found in the processes of formation of PCP-structures from diphosphines (see Table 4 and Section II.2.a). For instance, metallation of the aliphatic (in the HL[27] ligand) and vinylic fragments (in the diphosphines HL[10] and HL[45]) is markedly hampered as the chloride-containing palladating reagent is replaced by bromide- and then by iodide-containing analogues.[60, 61]

The observed halide effects may suggest a similar electrophilic mechanism for cyclopalladation of both phosphites and phosphines. However, assuming that the overall reaction rate is determined by the stage of C−H bond activation in the coordination precursors with similar structures and taking into account the increase in the basicity of the metallic centre in the series $I^- < Br^- < Cl^-$,[269] one can conclude that the halide effect

observed experimentally attests to the nucleophilic rather than electrophilic behaviour of the metal. An alternative interpretation of the halide effect is the increase in the *trans* influence of halides in the sequence $Br^- < Cl^-$;[270] as a result, the coordination site becomes vacant more readily due to weakening of the bond with the *trans*-ligand.

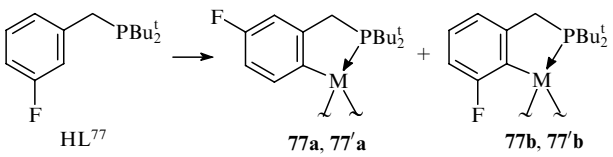
This criterion cannot be accepted as being perfect either, because the electronic and steric factors can influence the reaction mechanism in different ways, depending on the nature of P-donor ligands. With lower steric requirements of the ligands (phosphites are usually characterised by smaller Tolman cone angles[95, 107, 271]), electronic effects acquire primary importance, whereas for bulky phosphines, steric effects are more significant. In this case, the size and the leaving-group properties of the halide ion become more important and dissociation of one of the ligands with the formation of a coordination vacancy may become the rate-determining step.[272]

From determination of the protonation enthalpy for metal complexes, it is known that the appearance of the hydride ligand in the coordination sphere results in a sharp increase in the metal basicity: it can be 20 kcal mol^{-1} higher than that for analogous halide complexes.[269] During cyclopalladation through hydride intermediates, the opposite pattern of dependence of the reaction rate on the nature of the anions is observed: the formation of palladacycles from the $[PdH(X)(PBu^t_3)_2]$ precursors (X = Cl, Br, CF_3COO) is substantially accelerated in the sequence $CF_3COO^- < Cl^- < Br^-$.[71, 171] This type of dependence can be interpreted as indicating a nucleophilic pathway. It is assumed that in these reactions, direct intramolecular elimination of a hydrogen molecule (rather than an HX molecule) formed from the hydride ligand and one of the phosphine hydrogen atoms (forcibly located close to the metal) can take place.[71]

A similar dependence on the nature of the halides has been observed in the intermolecular activation of aliphatic C–H bonds of cyclohexane by the $[Pd(PPh_3)_2Hal_2]$ complexes.[161, 162] The hydride species $[CyPd^{IV}(H)(PPh_3)_2Hal_2]$ formed upon the oxidative addition were identified by spectroscopy; upon the subsequent reductive elimination of HHal, they were transformed into more stable $[CyPd^{II}(PPh_3)_2Hal]$ complexes.[162] The feasibility of this pathway in intermolecular processes has been confirmed by calculations.[229, 234]

The probability of the nucleophilic pathway should also increase in the cyclometallation with organoelement reagents containing Pd–R bonds[14] (see Section II.2.b). The fact that the hydride intermediate containing Pd(IV) (the product of oxidative addition of the C–H bond) has not been detected does not eliminate the possibility of such pathway, because these compounds are highly reactive and should easily undergo the reductive elimination of the hydrocarbon.

A convenient criterion for elucidation of the mechanism is the regiochemistry of reactions of substrates containing several alternative sites.[238] The only study of this kind known in the chemistry of cyclopalladation of P-donor ligands is the analysis of the isomeric composition of the phosphametallacycles formed by *m*-fluorobenzylphosphine HL^{77} (see Ref. 272). Upon the introduction of an electron-withdrawing substituent (in this particular case, fluorine) into the aromatic ring, the electron density in the ring markedly decreases, especially in the *ortho*-positions, one of which is to be attacked predominantly by a nucleophilic metal ion (for example, Ir^I, Rh^I). Conversely, in the case of an electrophilic mechanism, the C–H bond located in the *para*-position to the electronegative substituent should be attacked predominantly; exactly this outcome (the formation of only the *para*-isomer **77a**) was obtained in the reaction of the phosphine HL^{77} with Na tetrachloropalladate. When phosphines are metallated by compounds of electron-enriched monovalent iridium and rhodium, mixtures of *ortho*- and *para*-isomers (*o*-**77′b** and *p*-**77′a**) are formed in a 4 : 1 ratio.[272]



M = Pd (**77a**, 100%; **77b**, 0%); M = Ir (**77′a**, 20%; **77′b**, 80%)

Indirect evidence for the electrophilic mechanism of *ortho*-palladation of other benzylphosphines is provided by acceleration of the process upon the introduction of electron-donating substituents into the aromatic ring of the ligand.[14] For example, the formation of a phosphapalladacycle from benzyldi(*tert*-butyl)-phosphine (HL^{22}), with the unsubstituted aromatic ring, without assistance by a base requires long-term (5 days) refluxing of the intermediate chloride coordination complex in MET.[82] If the aromatic ring is modified by a crown-ether fragment (with electron-donating alkoxy groups in positions 3 and 4), the reaction becomes possible even at 20 °C.[113] The introduction of electron-donating substituents into the aromatic ring is especially efficient in the case of sterically non-crowded phosphines. For example, attempts to accomplish *ortho*-palladation of the phosphine $PhCH_2PPh_2$ (HL^{36}) failed during a long period,[82] whereas the 3,4-dimethoxy-substituted analogue HL^{65} reacts with an almost quantitative yield (91% in the step of C–H bond activation).[113]

It has been assumed[272] that substituents in the aromatic ring of benzylphosphines can also influence the charge and, hence, the reactivity of the metal; however, the transfer of electronic effects through the methylene group appears rather problematic. It can be considered that their influence is mainly limited to the aromatic C–H bond subjected to activation.

As opposed to cyclopalladation of benzylphosphines, *ortho*-palladation of phosphites of the type $4\text{-}RC_6H_4OP(OEt)_2$ (R = MeO, Me, NO_2) virtually does not depend on the electronic properties of the *para*-substituent in the aromatic ring: the product yields in the activation step of the C–H bond under comparable conditions remain unchanged (90% – 97%)[56] (see Table 1).

It can be suggested that this lack of sensitivity to the nature of the substituent in the aromatic ring can be related to the π-acceptor properties of the phosphites,[51, 53] whose P-coordination results in a sharp decrease in the electron density on the metal centre, thus facilitating the electrophilic attack. Indeed, the phosphites $P(OPh)_3$ and $P(OTol\text{-}o)_3$ have very low basicities (pK_a values are −2.00 and −1.83, respectively[53]). No data for $P(CH_2Ph)_3$ are available, but it follows from the pK_a values for $P(OPr^i)_3$ and $P(CH_2Pr^i)_3$ (4.08 and 7.97, respectively[53]) that the basicity decreases by four orders of magnitude upon the replacement of the methylene group present in the phosphine by the oxygen atom (in the phosphite ligand). Recall that the electrophilic mechanism is also assumed for the cycloplatination of phosphites.[17, 237]

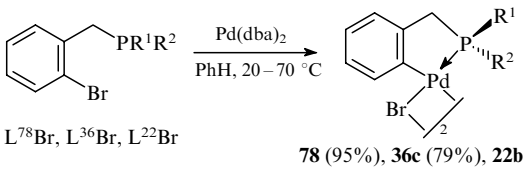
In conclusion, it should be noted that the mechanisms of cyclopalladation of P-donor ligands have not been adequately studied and further research along this line can provide a lot of interesting results.

III. Synthesis of phosphapalladacycles by oxidative addition

An alternative way for the construction of phosphapalladacycles is oxidative addition of the C–Hal bonds of preliminarily functionalised substrates to zerovalent palladium. This method is less attractive due to the necessity of preparing these substrates; therefore, the number of relevant publications is moderate.

A classical example of this approach is the reaction of the $Pd(dba)_2$ complex (dba is dibenzylideneacetone) with *o*-bromobenzylphosphines $(o\text{-}BrC_6H_4CH_2)PR^1R^2$, resulting in the cyclopalladated complexes as μ-bromide dimers.[273, 274] In this case (unlike direct intramolecular activation of the C–H bonds), the

enhancement of the steric requirements of the P-donor fragment of the $L^{78}Br$, $L^{36}Br$ and $L^{22}Br$ ligands in the series PMePh ($\theta' = 96°$)† < PPh_2 ($\theta' = 97°$) < PBu^t_2 ($\theta' = 121°$) entails a decrease in the yields of cyclopalladated complexes from nearly quantitative to moderate.[273]

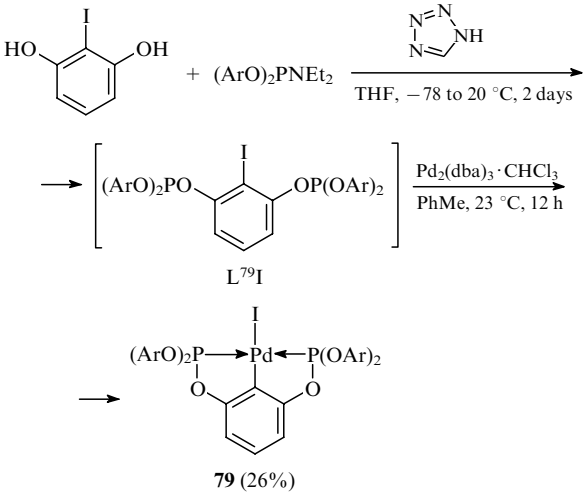


$L^{78}Br$, $L^{36}Br$, $L^{22}Br$ **78** (95%), **36c** (79%), **22b** (68%)

$R^1 = Me$, $R^2 = Ph$ ($L^{78}Br$, **78**); $R^1 = R^2 = Ph$ ($L^{36}Br$, **36c**); $R^1 = R^2 = Bu^t$ ($L^{22}Br$, **22b**).

This route to PC-palladacycles can be considered justified if the synthesis by direct activation of the C–H bond is either difficult (the μ-AcO analogue of the complex **36c** was obtained in ~20% yield) or impossible (for example, in the case of compound **78**).[114, 205]

The efficiency of the method based on oxidative addition for the creation of PCP-structures is difficult to estimate as the available information is sparse but, most likely, it is rather low. For example, in the synthesis of bis(phosphite) complex **79** by treatment of the 2-iodinated $L^{79}I$ ligand with $Pd_2(dba)_3 \cdot CHCl_3$, the overall yield over several steps (including generation of the ligand *in situ* from 2-iodoresorcinol) was only 26%.[275]



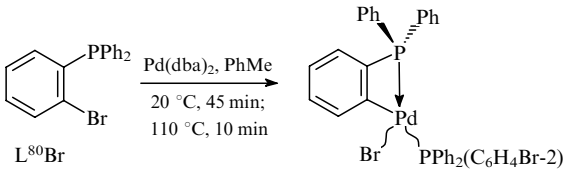
79 (26%)

Ar = 4-$MeOC_6H_4$.

This approach was even less efficient as applied to the synthesis of the bromide analogue of the PCP-complex **61a** from the diphosphine $L^{61}Br$: the yield in the proper oxidative addition step was only 19%.[165]

A rare example of direct activation of the C–H bond in triphenylphosphine with the assistance by fluoride ions in the cycloplatination has been reported.[276] A similar formation of a four-membered PC-palladacycle has been proposed earlier [170] for the reactions catalysed by the Pd(0)–PPh_3 system. However, the cyclopalladated structure of the resulting complex can hardly be considered established for the following reasons: (i) its alternative synthesis by direct activation of the *o*-C–H-bond in the coordination complex $[PdCl_2(PPh_3)_2]$ has been carried out under too mild conditions (AcOLi, DMF, 20 °C); (ii) the isolated compound was characterised only by elemental analysis and IR spectra.

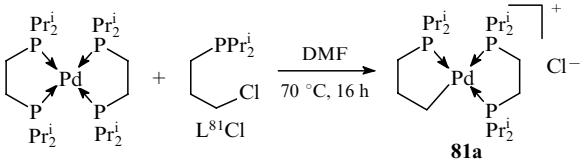
A four-membered PC-palladacycle sterically strained due to annelation to a benzene ring has been prepared only by using the oxidative addition of the *o*-bromo-substituted phosphine $L^{80}Br$ to Pd(0); the product structure was confirmed by X-ray diffraction analysis of the adduct *trans*-(P,P)-**80a**.[277]



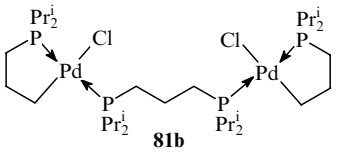
$L^{80}Br$ *cis*,*trans*-**80a** (53%)

The strained character of the metallacycle in **80a** is evident from the fact that in the absence of excess $L^{80}Br$ ligand, the reaction gives a macrocyclic tetranuclear compound with bridging (rather than chelating) PC-ligands — $[\{Pd(\mu\text{-}L^{80})(\mu\text{-}Br)\}_4]$, whose structure was confirmed by X-ray diffraction. Species of two types, those with μ- and η^2-bound ligand $(L^{80})^-$, exist in solutions in an equilibrium, whose position can be controlled by varying the auxiliary monodentate phosphines, in particular, bulky ligands stabilise the phosphapalladacycle, whereas in the presence of small-size phosphines (PMe_3, PMe_2Ph), the PC-palladacycle is cleaved giving rise to bi- or tetranuclear species.[277, 278] An attempt to elucidate the reaction mechanism by spectroscopic monitoring has shown only the intermediate formation of the coordination complex $[Pd(dba)(\kappa^1\text{-}L^{80}Br)_2]$.[277]

The scope of the method considered in this Section is not limited to reactions of aromatic $C(sp^2)$–Hal bonds. At least one example is known where the aliphatic PC-palladacycle is formed through oxidative addition of the $C(sp^3)$–Cl bond of the γ-chloropropylphosphine $L^{81}Cl$ to Pd(0) stabilised by 1,2-bis(diisopropylphosphino)ethane (dippe).[279]



Initially, compound **81a** was detected as a side product in attempted preparation of the $[Pd^0(dippp)_2]$ catalyst [280] from 1,3-bis(diisopropylphosphino)propane (dippp) contaminated by γ-chloropropylphosphine $L^{81}Cl$. The structure of the isolated binuclear complex **81b** with a bridging diphosphine was confirmed by X-ray diffraction.



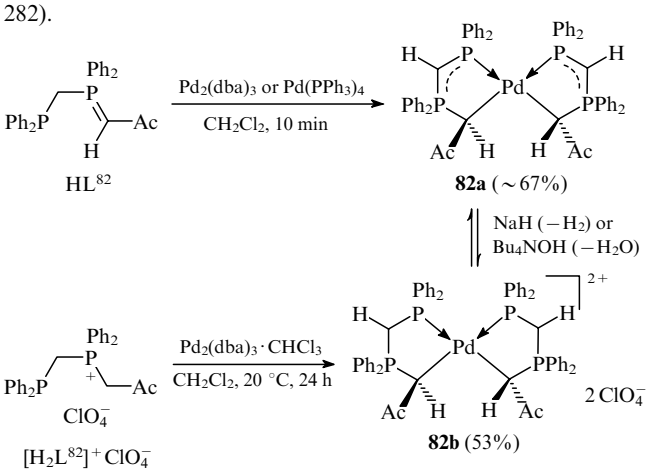
The researchers cited reasonably believe [279] that activation of the aliphatic C–Cl bond is promoted by the preliminary P-coordination of the substrate to the metal, because the rate of the intermolecular oxidative addition of butyl chloride to the same Pd(0) complex is lower by several orders of magnitude (even with excess alkyl halide and when the reaction is conducted under more drastic conditions, at 100 °C). This process may be additionally stimulated by the bulky diphosphines (dippp and dippe).

Thus, the method for the synthesis of PC (but not PCP) complexes by activation of the C–Hal bonds by palladium(0) is rather efficient, but the necessity of preliminary functionalisation of the phosphorus-containing substrate should be regarded as its drawback. The complication of the synthetic protocols could be avoided in the case of direct activation of the C–H bond by Pd(0) compounds.[281]

However, to the best of our knowledge, only one example of reaction of this type is known in the chemistry of complexes of zerovalent palladium, namely, the oxidative addition to Pd(0)

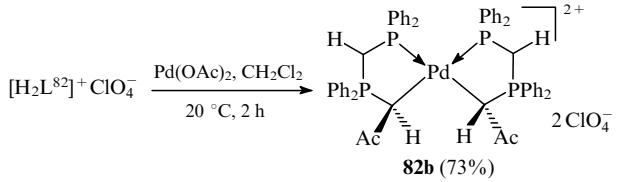
† From here on, the θ' value designates the contribution from the PR^1R^2 fragment to the Tolman θ angle.

complexes of the α-stabilised phosphino-P-ylide HL^{82} or its synthetic precursor, the phosphonium salt $[H_2L^{82}]^+$ (see Ref. 282).



In both processes, *cis*-bis(chelate) complexes are formed and molecular hydrogen is evolved, which was confirmed by gas chromatography. A significant distinctive feature of the former reaction is additional deprotonation of the phosphino-P-ylide ligand in complex **82a** compared to its formally neutral state in the analogue **82b** formed according to the latter pathway. The structural characteristics of the spiro complex **82a** obtained by X-ray diffraction analysis confirm both the methanide nature of the $\{PC(H)P\}^-$ fragment with the central sp^2-hybridised carbon atom and the substantial delocalisation of the electron density in this fragment. The transoid arrangement of two acetyl groups at the ylide carbon atoms (in the axial positions on opposite sides of the coordinate plane) points to a high diastereoselectivity of the formation of C* stereocentres, which are fixed in identical (*S*,*S*)- or (*R*,*R*)-configurations.

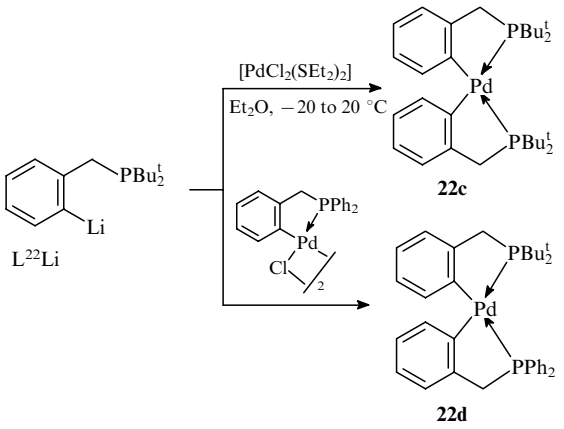
The true mechanism of these transformations is unknown, but a rough estimation of the reactivities of the two forms of the ligand used on the basis of the yields and reaction durations shows that the free phosphino-P-ylide HL^{82} is much more reactive in the oxidative addition than the phosphonium salt $[H_2L^{82}]^+ClO_4^-$. Note for comparison that direct activation of the C−H bond in the latter ligand under the action of $Pd(OAc)_2$ to give complex **82b** is more efficient (yield 73%).[282]



IV. Transmetallation

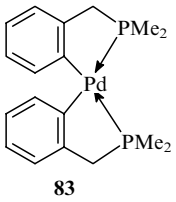
The transmetallation of lithiated phosphines on treatment with palladium(II) coordination complexes is a unique method for the synthesis of phosphapalladacycles as bis(chelate) compounds of the spiro structure.[16,283,284] Recall that direct intramolecular activation of the C−H bonds results in PC-palladacycles as μ-halide or μ-carboxylate dimers or their mononuclear derivatives (see Section II and Table 1).

The $[PdCl_2(SEt_2)_2]$ coordination complex serves usually as the source of palladium(II) in the stage of metal exchange; for example, it is used in the synthesis of spiro complex **22c** from the *ortho*-lithiated ligand HL^{22} (see Refs 283, 285).



The introduction of standard μ-chloride dimeric cyclopalladated complexes into the reactions with lithiated phosphines opens up the way to asymmetrical spiro structures both with identical (*e.g.*, complex **22d**) and with different donor atoms (P and N; see Table 2).[284,286,287] It has been assumed that mixed-ligand bis(chelate) compounds containing both soft and hard donor atoms at the same metallic centre can be of interest for catalysis.[287] However, as far as we know, their potential as (pre)catalysts has not been evaluated as yet.

Usually, reactions of this type proceed under mild conditions with rather high yields (60%−90%) and do not require steric stimulation.[283,284] For instance, this method was used to prepare complex **83** with the smallest donor groups, PMe_2,[283] whereas, attempts at direct activation of the aromatic C−H bond in dimethylbenzylphosphine (HL^{83}, $\theta = 134°$) have been unsuccessful.[288]



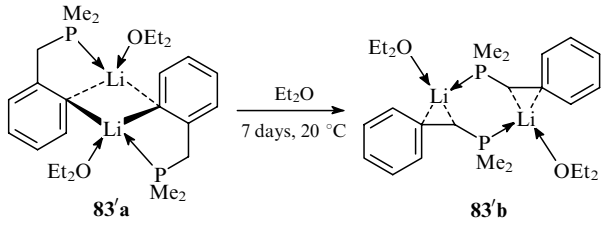
83

The practical value of these bis(chelate) PC-complexes increases due to the fact that they can be easily converted in high yields into standard dimeric cyclopalladated compounds with halide or acetate bridges.

In this version, transmetallation has been applied only to tertiary benzylphosphines, the preparation of *ortho*-lithiated ligands being the key problem. As opposed to tertiary benzylamines where (provided that no steric contraindications are involved)[289,290] direct activation of the $C(sp^2)-H$ bond in the benzene ring is possible and is widely used,[291−295] in the case of phosphorus analogues, direct *ortho*-lithiation proved to be impossible.[296,297] Therefore, a standard method for the synthesis of *ortho*-lithiated benzylphosphines is replacement of bromine by lithium,[298,299] which requires preliminary *ortho*-functionalisation of phosphine. However, in this case, too, the reactions of *ortho*-halogenated benzylphosphines with organolithium reagents can be complicated by at least two side reactions, namely, α-metallation and nucleophilic substitution at phosphorus (depending on the nature of the P-substituents, the nature of the halide, and the reaction conditions).[298,300] For example, *o*-chlorobenzylphosphines are metallated predominantly at the α-benzyl position, while the bromine atom in the *ortho*-position of the aromatic ring can be replaced by lithium almost quantitatively under appropriate conditions.[300−302] The susceptibility for α-lithiation can be illustrated by the replacement of the α-benzyl protons of all three

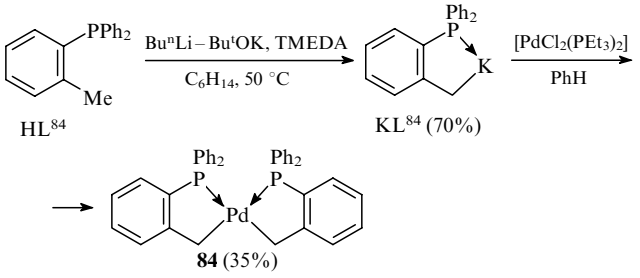
benzyl groups of the phosphonium salt $[PhP(CH_2Ph)_3]Cl$ in the reaction with BuLi.[303]

Detailed investigation of the behaviour of two *ortho*-lithiated benzylphosphines, $R_2PCH_2C_6H_4Li$-2 (R = Me, Ph), has shown that in donor-type solvents and in the presence of *N*,*N*,*N*′,*N*′-tetramethylethane-1,2-diamine (TMEDA), they are easily isomerised into the corresponding thermodynamically more stable α-lithiated derivatives *via* 1,3 proton migration. The structures of two isomeric products of lithiation of dimethylbenzylphosphine, **83′a** and **83′b**, were confirmed by X-ray diffraction.[299]



83′a **83′b**

For the synthesis of spiro complexes with the $C(sp^3)-Pd$ bond from *o*-tolylphosphines, an alternative approach involving the potassium salt of the ligand (for example, HL[84]) has been proposed.[304, 305] Among obvious advantages of this method, one should mention the possibility of direct metallation of the *o*-methyl group of the tolyl substituent. Butyllithium in the presence of TMEDA and an approximately equimolar amount of potassium *tert*-butoxide was used as the reagent.

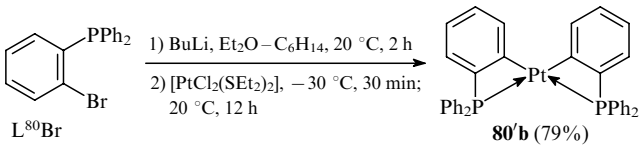


HL[84] KL[84] (70%)

84 (35%)

Presumably,[305] the success of metallation is determined by the exchange between two reagents, Bu^tOK and Bu^nLi, resulting in the formation of butylpotassium species. When Bu^tONa is used, the yields decrease to 40%, and in the presence of Bu^tOLi, metallation does not proceed at all.[305] For the synthesis of PC-palladacycles, the coordination complexes *trans*-$[PdQ_2Cl_2]$ are used (Q = PEt_3, SEt_2). This choice is determined by good solubility of these reagents, the volatility of the auxiliary ligands Q, and their indifference with respect to metallated KL ligands. Unfortunately, the yield of complex **84** obtained in this way did not exceed 35%.

All the above examples refer to the preparation of five-membered PC-palladacycles. In a recent study,[306] this method was used to prepare platinum(II) *cis*-spiro-complex **80′b** with two four-membered PC-metallacycles on the basis of the *ortho*-brominated triphenylphosphine $L^{80}Br$.

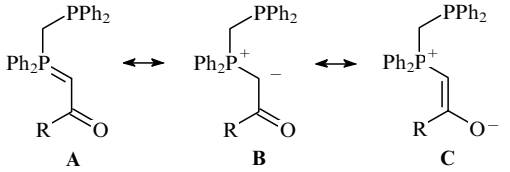


$L^{80}Br$ **80′b** (79%)

It is noteworthy that most of bis(chelate) spiro complexes of both PC- and NC-type[307] are formed as *cis*-isomers, which is explained by the 'antisymbiosis' effect,[308] namely, in transition metal complexes, the *trans*-arrangement of two 'soft' donor atoms markedly destabilises the system. However, in the case of mixed-ligand complexes with different donor atoms in two metallacycles (for example, of the PC and NC types), the formation of the *trans*-isomer is also possible, the isomer ratio being dependent on the order in which the metallacycles are closed.[284]

V. P,C-Chelation of phosphine-substituted phosphorus ylides

In the coordination chemistry of α-stabilised P-ylides, C-binding to soft metals, in particular, palladium and platinum, is usually preferred.[309] The functionalisation of these P-ylides by an additional phosphine fragment opens up the new route to the closure of phosphapalladacycles by simple chelation. A fundamental feature that distinguishes phosphino-P-ylides from other classes of ligands considered in this review is their zwitter-ionic structure, which imparts quasi-carbanionic properties to the ylide carbon atom (structure **B**) even before the reaction with the metal.[309, 310]

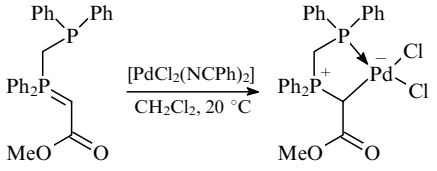


A **B** **C**

The presence of electron-withdrawing substituents (in particular, the carbonyl group) in the P-ylide molecule provides partial delocalisation of the negative charge of the ylide carbon with participation of the carbonyl oxygen (structure **C**), which makes ligands of this class rather stable in the free state and convenient to work with. An adverse consequence of this α-stabilisation is the somewhat reduced nucleophilicity of the ylide carbon; however, it remains sufficiently quasi-anionic to enable direct efficient binding to soft transition metals. Due to the presence of an additional phosphine group, the process of formation of PC-palladacycles is reduced to mere chelation of the zwitter-ionic ligand with Pd(II) compounds involving no activation of the C–H bond or deprotonation. The X-ray diffraction data available for complexes of this class[282, 311–314] clearly demonstrate that the greatest contribution to the electronic structure of the PC-bound phosphino-P-ylides is made by the bipolar canonical form **B**, whereas for free ligands, form **C** prevails.

Phosphino-P-ylide ligands are readily available; they are prepared by condensation of a diphosphine, namely, 1,1-bis(diphenylphosphino)methane (dppm) or dppe, with the corresponding α-halogen-substituted carbonyl compound of the $HalCH_2C(O)R$ type and subsequent deprotonation of the intermediate phosphino-phosphonium salt.[310, 315]

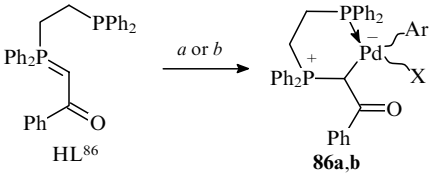
Cyclopalladated derivatives of phosphino-P-ylides are prepared using both preliminarily isolated ylide ligands and their precursors, phosphonium salts (see Table 3). The former version can be illustrated by the synthesis of the simplest monochelate dichloride complex **85a** by the reaction of phosphino-P-ylide L[85] with the benzonitrile reagent.



L[85] **85a** (80%)

The reaction is carried out under mild conditions and with high yields[315–317] almost irrespective of the size of the metallacycle to be formed (five- or six-membered) or the nature of the substituent R in the carbonyl fragment (R = Ph, Me, MeO, EtO). The monochelate P-ylide complexes of this type are thermally and oxidatively stable; compounds with five-membered PC-rings are more stable than those with six-membered rings; and the stability depends on the nature of the substituent R in the carbonyl fragment (Ph > Me > MeO).[317]

The same principle of simple chelation of phosphino-P-ylides is applicable to the synthesis of mono- and diaryl complexes **86a** and **86b**.[318] The corresponding binuclear complexes, [{ArPd.(μ-Hal)(THT)}$_2$] (THT is tetrahydrothiophene) or [Bu_4N]$_2$.[{Ar_2Pd(μ-Hal)}$_2$], are used as the reagents. In this case, too, reactions proceed under mild conditions and give products in satisfactory yields (60% – 80%).



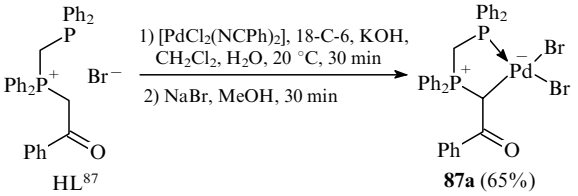
X = Cl, Ar = C_6Cl_5 (**86a**); X = Ar = C_6F_5 (**86b**);

(*a*) [{Pd(μ-Cl)(C_6Cl_5)(THT)}$_2$], PhH, 20 °C, 20 min, 69%;

(*b*) (Bu_4N)$_2$[{Pd(μ-Cl)(C_6F_5)$_2$}$_2$], Me_2CO, 20 °C, 30 min, 57%.

Asymmetrical monoarylated compounds such as **86a** are formed as mixtures of *trans*-C,C-/*cis*-C,C-isomers in 10 : 1 to 2 : 1 ratios.[318]

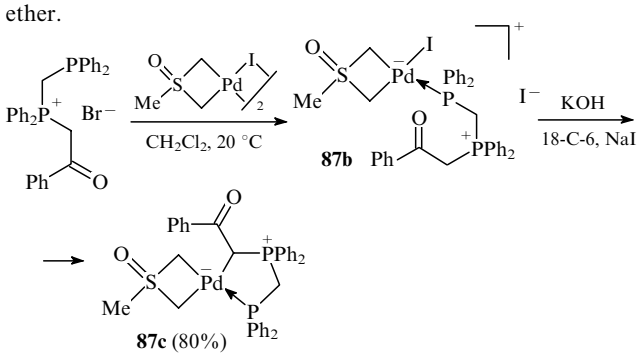
The synthesis of cyclopalladated derivatives of phosphino-P-ylides from the corresponding phosphonium salts [HL]$^+$X$^-$ is also reduced to direct chelation, as it implies generation of the P-ylide ligand *in situ* by deprotonation of the phosphonium precursor by a base. Since phosphonium bromides are normally used and an additional amount of bromide ions is introduced, phosphapalladacycles are formed as dibromide complexes (for example, **87a**).[313]



18-C-6 is 18-crown-6 ether.

The problem of solubility is solved by conducting the reaction in a two-phase system with the addition of 18-crown-6 ether (0.2 equiv.) as a phase transfer catalyst. The possibility of using less expensive reagents, for example, Na_2PdCl_4 can also be considered as an advantage. However, under any conditions (including experiments with a crown ether), the yields of the dibromide complex **87a** remained moderate (60% – 65%).

The phase transfer strategy has also been applied to prepare peculiar spiro complexes in which the metal is incorporated simultaneously into a five- or six-membered P-ylide phosphapalladacycle and a four-membered C,C-metallacycle formed by dianionic bis-S-ylides.[313] In this case, the PC-palladacycle (for example, that in the complex **87c**) is formed in a two-stage process through the intermediate monodentate P-coordination of the cationic [HL^{87}]$^+$ ligand to the S-ylide reagent and subsequent deprotonation under the action of a base in the presence of crown ether.

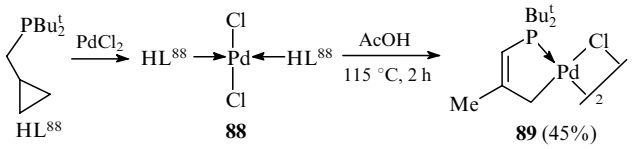


Although the yields of spiro complexes such as **87c** are, most often, relatively high (60% – 80%), the effect of the crown ether is still insignificant. Indeed, five-membered PC-palladacycles can be closed not only in the absence of a phase transfer catalyst but even without a base — due to the activation of the C – H bond with palladium. The structure of the complex **87c** was confirmed by X-ray diffraction data.[313]

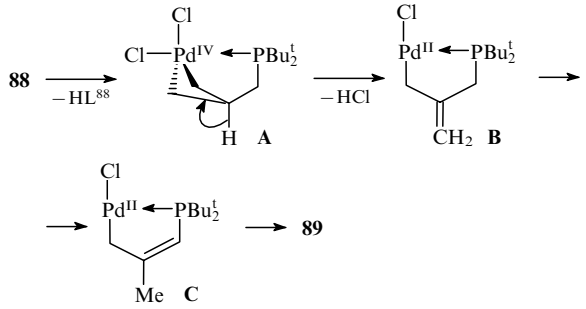
VI. Other routes to phosphapalladacycles

This Section describes a number of unusual transformations, giving rise to PC- or PCP-palladacycles due to activation of the C – C, C = P, C – F or C – O bonds; in these processes, the new ligand is formed on a metallic template.

The key step in the transformation of the cyclopropylmethylphosphine HL^{88} into the dimer **89** is the activation of the C – C bond in the strained cyclopropane ring in the coordination complex *trans*-[$PdCl_2(HL^{88})_2$] (**88**) during its thermolysis in glacial acetic acid.[319]



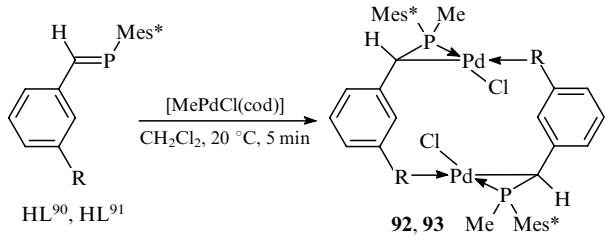
It is assumed [319] that the HL^{88} ligand is converted into dimer **89** by a route usual for the chemistry of cyclopropane.



The elimination of one of the phosphine ligands from precursor **88** is followed by activation of the C – C bond in the three-membered ring in the coordinatively unsaturated [$PdCl_2(HL^{88})$] species. The β-elimination of the proton from intermediate **A** yields phosphapalladacycle **B** with an *exo*-double bond; this product is then isomerised through a 1,3-hydride shift to form the PC-palladacycle **C** with an *endo*-double bond. The last-mentioned species further dimerises to give complex **89**.[319]

A similar process takes place at a platinum(II) centre;[320] meanwhile, in the reactions of the phosphine HL^{88} with iridium(I) [321] and di-*tert*-butyl(cyclobutylmethyl)phosphine with platinum(II),[321] the C – H bond of the small ring (retained in the final product) is subjected to activation.

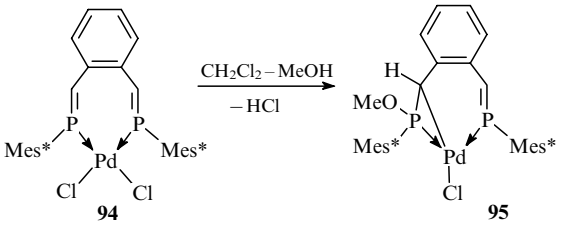
Unusual results have been obtained in a study of the reactions between the HL^{90} and HL^{91} phosphaalkene ligands and the organometallic reagent, [MePd(cod)Cl].[322] Although cyclometallated derivatives of phosphaalkenes of both PC- [117, 323] and PCP-types [117, 125, 127] are known (see Tables 1 and 4), these reactions were found to give three-membered PC-palladacycles under very mild conditions, instead of the expected cyclopalladated products of PC- or PCN-type with the optimal five-membered metallacycles or coordination complexes with P-mono- or P,N-bidentate ligands. One can see that the phosphaalkenes HL^{90} and HL^{91} with N-donor substituents R are converted into macrocyclic binuclear complexes **92** and **93** in high yields.



R = 2-Py (HL^{90}, **92**, 90%); R = CH=NPh (HL^{91}, **93**, 71%).

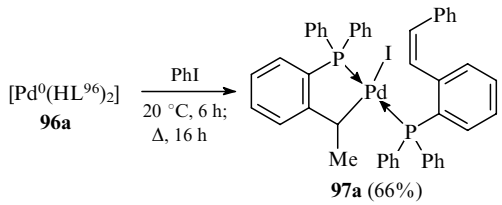
It has been suggested [322] that this process includes carbopalladation of the C=P bond in the starting ligand, *i.e.*, the formal addition of the Pd–Me fragment to the C=P double bond. The regiochemistry of the reaction complies with the polarisation of this bond ($C^{\delta-}=P^{\delta+}$) caused by the higher electronegativity of the carbon atom (2.5) compared to phosphorus (2.1):[324] the quasi-carbanionic methyl group attacks the phosphorus atom, while the metal goes to the carbon atom. Although the researchers do not discuss the stereochemistry of this process in which two stereocentres arise (C* and P*), the presence of only one signal in the ^{31}P NMR spectrum and only one set of ^{1}H NMR signals suggest that the reaction is highly diastereoselective. In the case of dimer **92**, this was confirmed by X-ray diffraction data: the crystal contains only enantiomeric three-membered PC-palladacycles of the (S_CR_P)- and (R_CS_P)-configurations.[322] It should be noted that despite the strained character of such structures, three-membered palladacycles with other heteroatoms, for example, CS- [325, 326] and CO-types are also known.[327]

Non-symmetrical bicyclic PCP-structures (for example, **95**) with annelated three- and six-membered PC-palladacycles and two chemically different P-donor centres (phosphaalkene and phosphinite ones) are formed in the reaction of the coordination complex **94** with alcohols. The regiochemistry of this process is also dictated by the inverted polarity of the $C^{\delta-}=P^{\delta+}$ bond (with respect to the polarity of the C=N bond): the nucleophilic attack by ROH occurs regioselectively involving only the $P^{\delta+}$ atom. This reaction is also diastereoselective; the formal *syn*-addition of the alcohol gives rise to two stereocentres with the same configuration, either (S_CS_P) or (R_CR_P).[328]

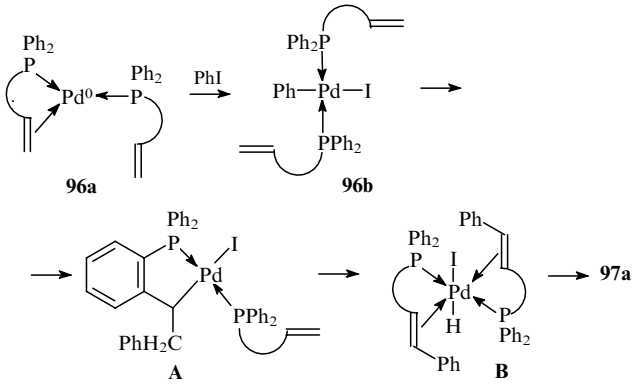


It should be noted that strained three-membered PC-metallacycles are also found in structures with other metals: Ru,[329, 330] Os,[331, 332] W,[333] and Ta [334] and so on.

The formation of a PC-palladacycle upon the reaction of iodobenzene and the Pd(0) complex with the (2-vinylphenyl)diphenylphosphine ligand HL^{96} is based on a complex sequence of transformations, resulting finally in the modification of the starting ligand (the structure of adduct **97a** was confirmed by X-ray diffraction [335]).



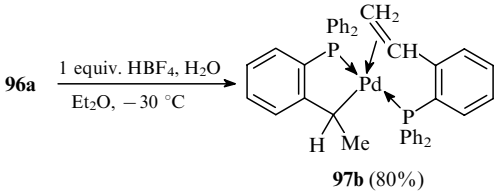
The process is assumed to start with the oxidative addition of PhI to the initial complex **96a** to give adduct **96b**, which appears quite reasonable in view of the coordinative unsaturation of the 16-electron particles. The migration of the metal-bound Ph group to the vinyl fragment of the monodentate P-coordinated HL^{96} ligand in intermediate **96b** gives rise to a new phenylated phosphine HL^{97} (*via* a transformation similar to the Heck reaction). Further, the HL^{97} ligand is closed to give a five-membered PC-palladacycle as adduct **A** with the starting phosphine HL^{96}.



The subsequent steps include β-elimination of hydrogen from the σ-bound alkyl group in the intermediate **A** to afford Pd(IV) hydride derivative **B** and, as the final step, the addition of the hydride to the olefinic fragment, which is either linked to the metal (or merely located close to the metal in space).[335]

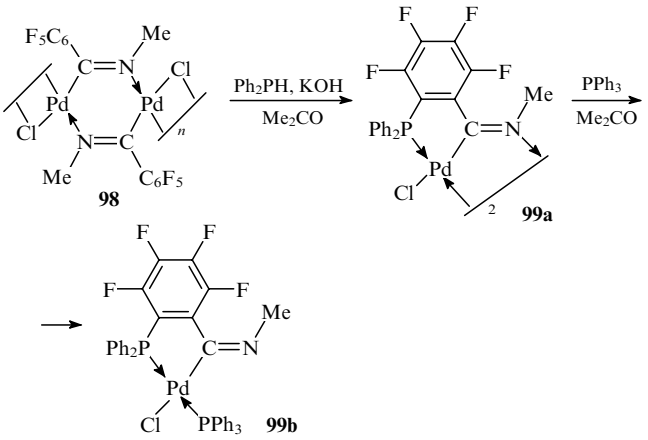
A similar cyclopalladated compound is also formed in the reaction of the complex **96a** with bromobenzene, whereas chlorobenzene is inactive in this process. The decrease in the reactivity of aryl halides in the sequence PhI ⩾ PhBr ≫ PhCl is typical of palladium-catalysed cross-coupling [336] and implies the crucial role of the oxidative addition of aryl halide.

An X-ray diffraction study of the starting complex **96a** has shown a shortened contact between Pd(0) and the α-hydrogen of the non-coordinated vinyl group of the phosphine HL^{96} (the Pd···H distance is 2.46 Å,[34] which is much shorter than the sum of the van der Waals radii of these atoms, equal to 3.1 Å, see Ref. 220). The attractive nature of this interaction seems obvious in view of both the displacement of the palladium atom toward the α-vinyl hydrogen by 0.22 Å and the existing way for a monodentately linked phosphine to avoid these contacts through rotation about the P–C bonds. Interactions of this type are usually considered as an intermediate step in the activation of the C–H bonds.[261, 262] Moreover, study of the temperature dependence of the ^{31}P NMR spectra of complex **96a** has shown that this complex exists in solutions in equilibrium with two-coordinate [Pd(κ^1-HL^{96})$_2$] species, the latter being the predominant form. Hence, the real state of the complex **96a** is nearly 14-electron, and this coordinative unsaturation should stimulate efficiently the oxidative addition. Indeed, treatment of the complex **96a** with an equimolar amount of aqueous HBF_4 under low-temperature conditions gives cationic cyclopalladated compound **97b** stabilised by η^2:κ^1-coordination of the non-metallated HL^{96} ligand.[34]

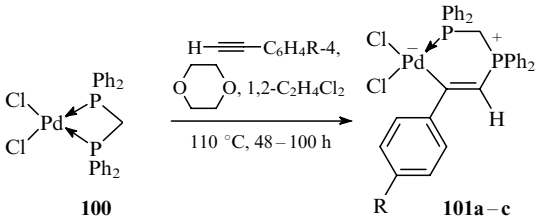


Yet another unusual route to the PC-palladacycle has been discovered in a study of reactions of polynuclear μ-imidoyl complex **98** with phosphides.[337] In this case, a new phosphine ligand is formed due to activation of the C–F bond in the C_6F_5 aryl group. The *ortho*-direction of the attack by the nucleophile (Ph_2P^-) is presumably caused by assistance by the metallic centre.

The product of this reaction, dimeric complex **99a**, differs from the analogues considered previously in that the bridging function is performed by the N-donor atoms of the C-metallated aldimine $(L^{99})^-$ rather than by the halide anions. The dimer **99a** is easily converted into mononuclear adducts (for example, complex **99b**) upon the reaction with auxiliary ligands. The initial compound **98** results from insertion of MeNC into the Pd–Ar bond of the organometallic reagent $[Pd(C_6F_5)_2(CNMe)_2]$ upon its interaction with $[PdCl_2(NCPh)_2]$.[338]

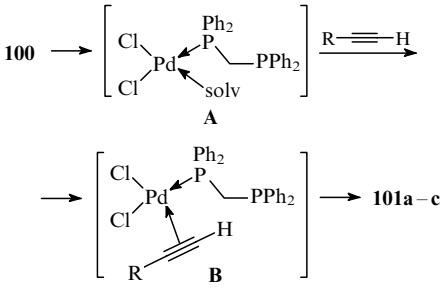


The formation of the P–C bond underlies an unusual pathway of the transformation of methylenediphosphine (dppm) into alkenyl phosphorus ylide ligands on a palladium(II) template.[339] The coordination complex **100**[340] with P,P-chelated diphosphine serves as the starting substrate. Long-term thermolysis of this compound in the presence of excess terminal alkyne yields complexes **101a–c** with zwitter-ionic phosphonium-alkenyl-P-ylide ligands, which possess high stability (thermal, oxidative and hydrolytic).



R = NMe_2 (**101a**, 31%), Ph (**101b**, 49%), NO_2 (**101c**, 73%).

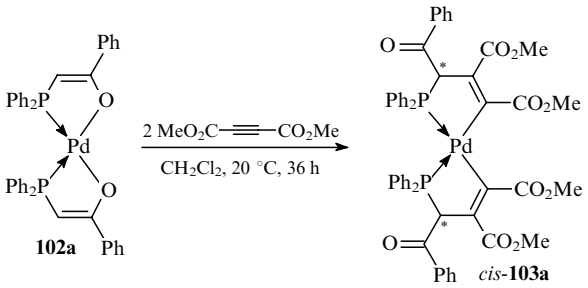
Reactions of this type are regiospecific: the Pd–C bond is formed only with the terminal carbon atom of the monosubstituted alkyne. This regiochemistry may be due to the substantial steric crowding of the reacting P-donor atom of the diphosphine and relatively slight shielding of the metallic centre (disubstituted alkynes cannot be introduced in this process). Although this reaction looks formally to be the insertion of the alkyne into the Pd←P bond, the researchers proposed a more realistic mechanism including (i) solvolytic dechelation of diphosphine in complex **100** to give coordinatively unsaturated species **A**; (ii) η^2-binding of alkyne to the metal at the newly formed coordination vacancy;



(iii) nucleophilic attack of the free PPh_2 group of the monodentate phosphine in intermediate **B** on the π-coordinated alkyne.

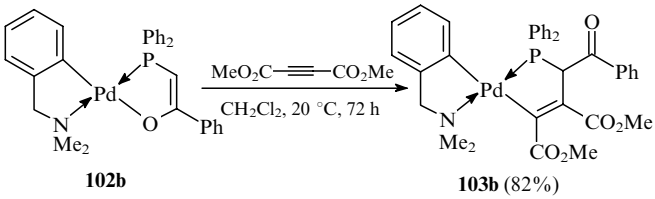
A number of experimental observations are consistent with this scheme. First, the reaction occurs only in the complex with dppm, which forms a strained (and, hence, unstable) four-membered chelate ring.[341] Transformation of this type proved impossible for the similar $[PdCl_2(dppe)]$ complex with diphosphine which forms a stable five-membered chelate ring. Second, the success of this transformation depends appreciably on the coordination capacity of the solvents used, which is important for dechelation of diphosphine: the reaction proceeds only in the presence of dioxane. Third, the coordination of alkynes to the metal should make them more susceptible to the nucleophilic attack. This is consistent with the regular increase in the reactivity of alkynes of the $4\text{-}RC_6H_4C{\equiv}CH$ type following the introduction of electron-withdrawing substituents R (Me_2N < H < NO_2) in the aromatic ring (the yields of complexes **101a–c** increase in this series).[339] A similar process proved possible for platinum(II) complexes with dppm.[342]

Alkenyl phosphametallacycles can be constructed from anionic β-phosphino enolates P,O-chelated to palladium through the formation of a new C–C bond.[343–345] The specific reactivity of ligands of the $R^1_2PCH{=}C(R^2)O^-$ type is due to high nucleophilicity of the carbon atom adjacent to phosphorus. Experiments were carried out with two spiro complexes of phosphino enolates, namely, the symmetrical bis(chelate) coordination compound **102a** and mixed-ligand analogue **102b** containing a CN-metallacycle.[346] Bis(chelate) **102a** reacts with dimethyl acetylenedicarboxylate to give spiro complex *cis*-**103a** of the alkenyl type containing a $C(sp^2)$–Pd bond.[343, 344]

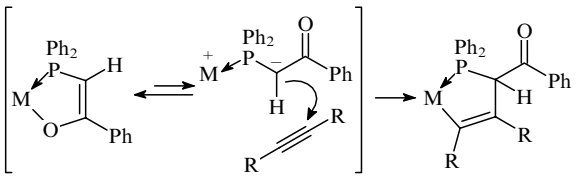


The stereoselectivity of this process, which gives rise to a C*-stereocentre in each of the metallacycles, is relatively low: complex **103a** is formed as a mixture of two diastereomers (3 : 1) with the same geometric *cis*-P,P-configuration. The predominant *meso*-form was isolated from the mixture by fractional crystallisation and characterised by X-ray diffraction.[343]

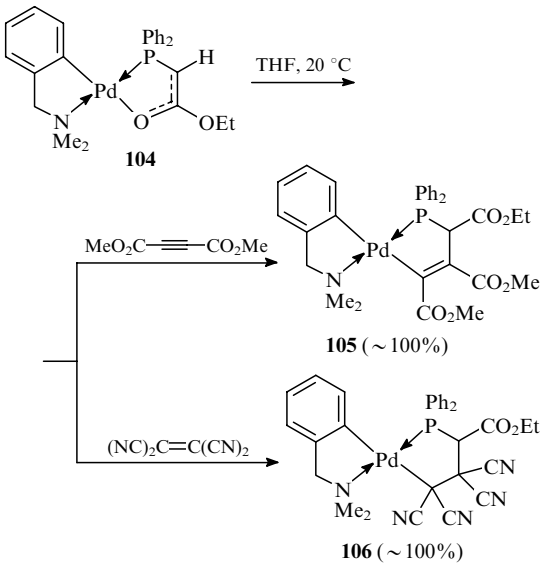
The same phosphapalladacycle as a part of a mixed-ligand spiro complex **103b** is formed in the reaction of alkyne with a phosphino enolate P,O-chelated to the benzylaminate CN-palladacycle (**102b**).[344, 345]



The mechanism of C–C-coupling of the enolate fragment of the P,O-bound ligand with the alkyne triple bond has not been studied. The activating role of the metallic centre is evident from the dependence of the reactivity of complexes on the nature of the metal (Ni > Pd > Pt). β-Phosphino enolates may be activated towards nucleophilic attack upon dechelation and tautomerisation to the keto form $M^+ \leftarrow PPh_2CH^-C(=O)Ph$, in which the α-carbon atom at phosphorus has a more pronounced carbanionic nature.[343–345]



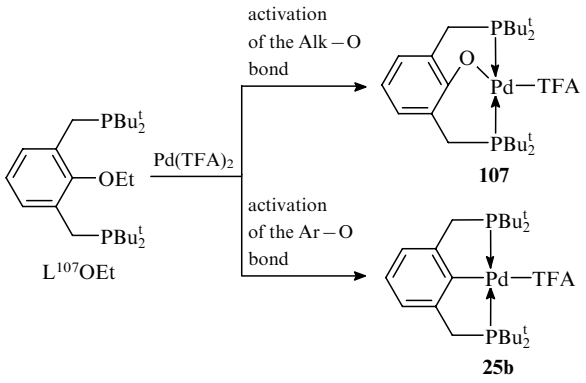
This suggestion seems quite reasonable from general considerations: the Pd—O bond between the 'soft' metal and the 'hard' oxygen donor atom cannot be strong. The dissociative mechanism is supported indirectly by a sharp acceleration of the process when carried out in an efficiently coordinating solvent. Thus complex **104** with a modified P,O-ligand reacts instantaneously with dimethyl acetylenedicarboxylate in THF to give spiro complex **105**,[345] whereas a similar reaction involving complex **102b** in dichloromethane proceeds to completion in 72 h.[344]



The reaction of complex **104** with an electron-deficient alkene (tetracyanoethylene) gives a phosphapalladacycle **106** of the alkyl type with the C(sp^3)—Pd bond whose structure was confirmed by X-ray diffraction.[345]

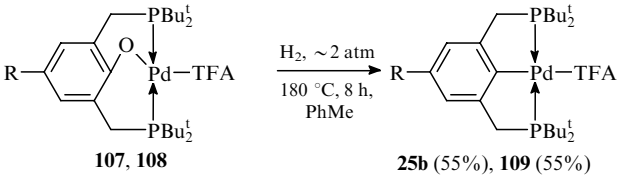
By contrast with homoleptic spiro complexes of type **103a**, which are formed as *cis*-C,C-isomers (but are completely isomerised into thermodynamically more stable *trans*-isomers on long-term heating),[344] their mixed-ligand analogues **103b**, **105** and **106** have initially the *trans*-C,C-geometry, which is at variance with the 'antisymbiosis' concept,[308] according to which the *trans*-arrangement of two soft donor atoms at a soft metallic centre destabilises the system.

The method for the synthesis of PCP-structures from derivatives of 2,6-bis(phosphinomethyl)phenols developed by Milstein [151, 347] seems fairly unusual, if one takes into account the high strength of the Ar—O bonds. Although this transformation can be easily performed on rhodium(I) centres, in the case of Pd(II), an attack on the weaker ArO—Alk bond to give phenoxy complexes is preferred under similar conditions (the structure of one of such complex has been confirmed by X-ray diffraction).[151] Also surprising is the effect of the minor modification of the alkyl group in the phenol ether on the direction of reaction with palladium(II) trifluoroacetate. Whereas in the case of the methyl ether L^{107}OMe, no cyclopalladation signs were found, in the case of ethyl-substituted analogue L^{107}OEt, $Pd(TFA)_2$ reacts along two competing pathways to give products of the formal insertion of the metal into the ArO—Alk (**107**) and Ar—OAlk (**25b**) bonds in the kinetically controlled 9 : 1 ratio, *i.e.*, the former pathway remains preferred.[151]



The differences in the behaviour of analogous substrates, L^{107}OMe and L^{107}OEt, have been attributed [151] to steric effects. Since the mechanism of the formation of phenoxy complex **107** postulated by these researchers includes an S_N2 attack by the anion (here, the $CF_3CO_2^-$ group) on the alkyl group of the ether, the replacement of the MeO group by the EtO group makes the nucleophilic attack on the α-carbon atom sterically more hindered, which opens up the way for competing cyclopalladation.

The POP-phenolate complexes **107** and **108** predominating in these processes can be converted into cyclometallated PCP-structures **25b** and **109** by long-term thermolysis in a hydrogen atmosphere, resulting in activation of the Ar—O bond.[151]



R = H (**107**, **25b**), Me (**108**, **109**).

Presumably, the mechanism of this process includes opening of the ArO—Pd σ-bond under the action of excess hydrogen, and the phenol ArOH thus formed participates further in two competing reactions, namely, reversible activation of the O—H bond and irreversible activation of the Ar—O bond, the latter being responsible for the closure of the phosphapalladacycles. Unusual as it may seem, this hydrodeoxygenation process is of no preparative value, because these products are available *via* direct activation of C—H bonds under mild conditions (see Table 4).

VII. Supplement

Table 1. Phosphapalladacycles of the PC-type.

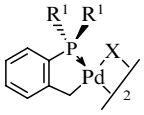
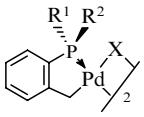
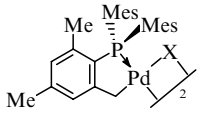
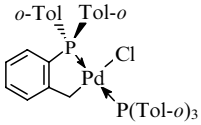
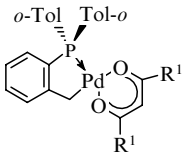
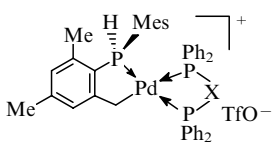
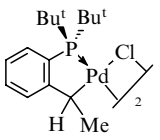
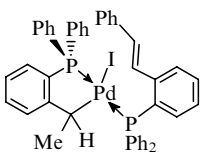
Complex [a]	Designation of the compound	X	R^1	R^2	Reagents and reaction conditions	Yield [b] (%)	Ref.
PC-Complexes with the C(sp^3)—Pd bond							
	**29a** [c]	AcO	*o*-Tol		1) $Pd(OAc)_2$ – P(Tol-*o*)$_3$ (1 : 1.3), PhMe, 50 °C, 3 min 2) $Pd(OAc)_2$ – P(Tol-*o*)$_3$ (1 : 1), Me_2CO, Δ, 1 h	93 79	8 [c], 10 148
	29d	TFA	*o*-Tol		$Pd(TFA)_2$ – P(Tol-*o*)$_3$, PhMe, 20 °C, 6 h	–	348
	29e [c]	I	*o*-Tol		$Pd(OAc)_2$ – P(Tol-*o*)$_3$, Et_3N, ArI, diene	–	349, 350 [c]
	21a	Cl	Bu^t		(*a*) Na_2PdCl_4 – P(Tol-*o*)Bu^t_2 (1 : 2), MeOH, −6 °C, 45 min; (*b*) Na_2PdCl_4 (1 equiv.), EtOH – MeOH, Δ, 5 min	76 [d] (90)	81
	21b	AcO	Bu^t		$Pd(OAc)_2$ – P(Tol-*o*)Bu^t_2 (1 : 1), PhMe, 20 °C, 6 h	90	10
	32	AcO	Cy		$Pd(OAc)_2$ – P(Tol-*o*)Cy_2 (1 : 1), PhMe, 20 °C, 12 h	41	10
	**30a** [c]	AcO	*o*-Tol	Bu^t	$Pd(OAc)_2$ – P(Tol-*o*)$_2Bu^t$ (1 : 1), PhMe, 60 °C, 5 min	94	10, 147 [c]
	30b	Cl	*o*-Tol	Bu^t	1) Na_2PdCl_4 – P(Tol-*o*)$_2Bu^t$ (1 : 1), PrOH – MeOH, Δ, 3 min; 2) (*a*) Na_2PdCl_4 – P(Tol-*o*)$_2Bu^t$ (1 : 2), EtOH – MeOH, 20 °C, 30 min; (*b*) Pr^nOH, Δ, 3 min 3) (*a*) Na_2PdCl_4 – P(Tol-*o*)$_2Bu^t$ (1 : 2), EtOH – MeOH, 20 °C, 30 min; (*b*) Na_2PdCl_4 (1.2 equiv.), MeOH, 50 °C, 2 min; Pr^nOH, Δ, 5 min 4) (*a*) K_2PdCl_4 – P(Tol-*o*)$_2Bu^t$ (1 : 1), CH_2Cl_2 – H_2O, 40 °C, 5 min; (*b*) Bu^iOH, Δ, 7 min 5) [{Pd(η^2-$C_6H_4CH(Bu^t)NH_2$-2)(μ-Cl)}$_2$] – P(Tol-*o*)$_2Bu^t$ (1 : 2), PhMe – AcOH, 60 °C, 1 h	97 84 [d] (96) 85 [e] (97) 94 [f] 71	81 81 81 145 206, 207
	31	AcO	*o*-Tol	Cy	$Pd(OAc)_2$ – P(Tol-*o*)$_2$Cy (1 : 1), PhMe, 20 °C, 6 h	42	10
	**35a** [c]	Cl			1) $[PdCl_2(NCPh)_2]$ – $PMes_3$ (1 : 2), CH_2Cl_2, 20 °C, 30 min 2) $[PdCl_2(NCPh)_2]$ – $PMes_3$ (1 : 1), CH_2Cl_2, 20 °C, 30 min 3) $PdCl_2$ – $PMes_3$ (1 : 2), CH_2Cl_2, 20 °C, 8 – 10 h	98 94 ~75	109, 110, 351 [c] 110 110
	35b	AcO			$Pd(OAc)_2$ – $PMes_3$ (1 : 1), PhMe, 20 °C, ~12 h	81	10
	**29f**				$[PdCl_2\{P(Tol\text{-}o)_3\}_2]$, AcOLi, AcOH, H_2, Δ, 2 h	–	170
	**29b**		CF_3		1) (*a*) $[Pd(hfac)_2]$ – P(Tol-*o*)$_3$ (1 : 1), hexane, Δ; (*b*) CH_2Cl_2, 20 °C, 10 days 2) $[Pd(hfac)_2]$ – P(Tol-*o*)$_3$, PhH, Δ	40 [g] (47) –	196 116
	29g		Me		$Pd(acac)_2$ – P(Tol-*o*)$_3$, PhH, Δ	–	116
	**71b** [c]	CH_2CH_2			(*a*) [Pd(dppe)(Me)Cl] – $PHMes_2$ (H_2L^{71}) – AgOTf (1 : 1 : 1), MeCN – THF, 1 h; (*b*) Me_2CO, HOTf (1 equiv.), 60 °C, 3 days	68 [h] (85)	169
	71c	CH=CH			(*a*) [Pd(dppen)(Me)Cl] – $PHMes_2$ (H_2L^{71}) – AgOTf (1 : 1 : 1), MeCN – THF, 15 min; (*b*) THF, 60 – 65 °C, 3 days	59 [h] (63)	352
	**1**				(*a*) Na_2PdCl_4 – HL^1 (1 : 2), MeOH – EtOH, 20 °C, 1 h; (*b*) Pr^nOH, Δ, 20 min	83 [d] (~100)	55
	**97a** [c]				(*a*) [Pd(η^5-Cp)(η^3-All)] – HL^{96} (1 : 2); (*b*) PhI (excess), PhH, 20 °C, 6 h; 80 °C, 16 h	see [i] (66)	335

Table 1 (continued).

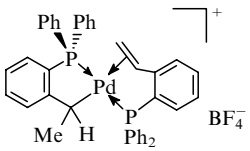
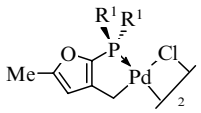
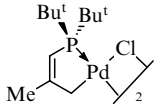
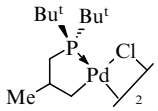
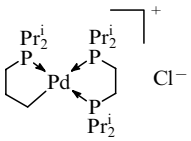
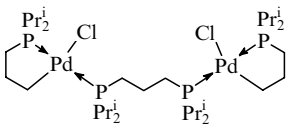
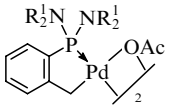
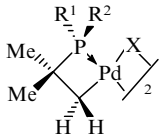
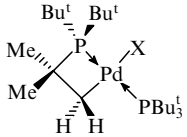
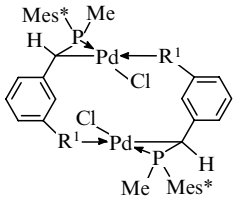
Complex [a]	Designation of the compound	X	R^1	R^2	Reagents and reaction conditions	Yield [b] (%)	Ref.
PC-Complexes with the $C(sp^3)-Pd$ bond							
	**97b**				(*a*) [Pd(η⁵-Cp)(η³-All)] – HL^{96} (1 : 2), PhMe, 20 °C, > 3 h; (*b*) $HBF_4 - H_2O$ (1 equiv.), Et_2O, −30→20 °C	52 [i] (80)	34
	**110**		3,5-Me_2-2-furyl		$[PdCl_4]^{2-}$ – HL^{110}, MeOH $HL^{110} = PR^1_3$	–	353
	**89** [c]				(*a*) $PdCl_2$ – HL^{88} (1 : 2), EtOH – H_2O, 20 °C, 3 days; (*b*) AcOH, Δ, 2 h	43 [d] (45)	319
	**42**				(*a*) Na_2PdCl_4 – $PBu^t_2Bu^i$ (1 : 1), EtOH, Δ, 0.5 h; (*b*) MET, Δ, 23 h	40 [f] (48)	119
	**81a**				$[Pd^0(dippe)_2]$ – $Pr^i_2P(CH_2)_3Cl$ (1 : 1), DMF, 70 °C, 16 h (in a sealed tube)	–	279
	**81b** [c]				[{Pd(η³-CH_2=$CMeCH_2$)(μ-Cl)}₂] – dippp – $L^{81}Cl$ (1 : 1 : 2), MeO^-, MeOH – PhMe	< 50 [j]	279
	**111**		Me_2		$Pd(OAc)_2$ – (Tol-*o*)$P(NMe_2)_2$, PhMe, Δ, 2 h	~90	354
	112		$(CH_2)_4$		$Pd(OAc)_2$ – (Tol-*o*)$P\{N(CH_2)_4\}_2$, PhMe, Δ, 2 h	~90	354
	113		$(CH_2)_5$		$Pd(OAc)_2$ – (Tol-*o*)$P\{N(CH_2)_5\}_2$, PhMe, Δ, 2 h	~90	354
	**20a** [c]	Cl	Bu^t	Bu^t	1) K_2PdCl_4 – PBu^t_3 (1 : 2), DMF, 20 °C, 12 h	72	69, 70, 149 [c], 355 [c]
					2) Na_2PdCl_4 – PBu^t_3 (1 : 3), DMF, 20 °C, 48 h	75	73
					3) $[PdCl_2(NCPh)_2]$ – PBu^t_3 (1 : 2), CH_2Cl_2, 20 °C, 2 h	70	70
					4) $[PdCl_2(NCPh)_2]$ – PBu^t_3 (1 : 1), CH_2Cl_2, 20 °C, 2 h	> 80	71
					5) [{$Pd(PBu^t_3)Cl(\mu\text{-}Cl)$}₂] – AgOAc (1 : 2), $CHCl_3$, 20 °C, 12 h	~100	83, 84
					6) [{(η² : η¹-Z)Pd(μ-Cl)}₂] – PBu^t_3 (1 : 2), MeOH, 20 °C, 2 h; Z^- = 2-MeO-cycloocten-5-yl	80	74
	20f [c]	Br	Bu^t	Bu^t	$[Pd^I_2(PBu^t_3)_2(\mu\text{-}Br)_2]$ – O_2, PhH, 20 °C	traces	356
	23	Cl	Bu^t	Ph	(*a*) Na_2PdCl_4 – PBu^t_2Ph (1 : 2), MeOH, 20 °C, 1 h; (*b*) Na_2PdCl_4 (1 equiv.), EtOH – Et_2O, Δ, 1 h; (*c*) AgOAc (2 equiv.), $CHCl_3$, 20 °C, 12 h	43 [k] (55)	83, 84
	**20c**	Cl			1) $[PdCl_2(cod)]$ – PBu^t_3 (1 : 2), PhH, 20 °C, 8 days	–	69
					2) (*a*) $[Pd^0(PBu^t_3)_2]$, HCl – Et_2O, 20 °C; (*b*) PhH – EtOH, 0.5 h	> 80 [l]	71, 171
	20e	TFA			(*a*) $[Pd^0(PBu^t_3)_2]$, TFAH, Et_2O, 20 °C; (*b*) PhH – EtOH, 3 h	> 80 [l]	71, 171
	**92** [c]		2-Py		$[MePdCl(cod)]$ – 3-$R^1C_6H_4CH$=PMes* (1 : 1), CH_2Cl_2, 20 °C, 5 min	90	322
	93		CHN=Ph		$[MePdCl(cod)]$ – 3-$R^1C_6H_4CH$=PMes* (1 : 1), CH_2Cl_2, 20 °C, 5 min	71	322

Table 1 (continued).

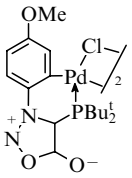
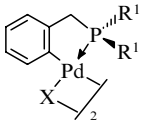
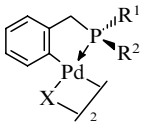
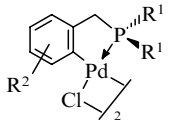
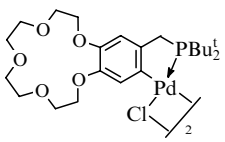
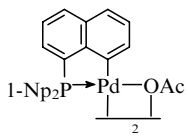
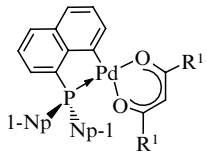
Complex [a]	Designation of the compound	X	R^1	R^2	Reagents and reaction conditions	Yield [b] (%)	Ref.
PC-Complexes with the $C(sp^2)-Pd$ bond							
	**13** [c]				$PdCl_2$ – HL^{13} (1 : 1), HCl(conc.) – EtOH (1 : 1), 80 °C, 4 h	74	63
	**22a**	Cl	Bu^t		1) (*a*) Na_2PdCl_4 – PBu^t_2Bn (1 : 2), MeOH, 20 °C, 3 h; (*b*) MET, Δ, 5 days	49 [d] (68)	82
					2) (*a*) Na_2PdCl_4 – PBu^t_2Bn (1 : 2), MeOH, 20 °C, 3 h; (*b*) AcONa (excess), MET, Δ, 0.5 h	72 [d] (100)	82
					3) (*a*) Na_2PdCl_4 – PBu^t_2Bn (1 : 2), MeOH, 20 °C, 3 h; (*b*) Et_3N, decalin, Δ, 17 h	46 [d] (64)	82
	22b	Br	Bu^t		1) $[Pd(dba)_2]$ – $L^{22}Br$ (1 : 1), PhH, 20 °C, 1 h; 40 °C, 1 h; 70 °C, 0.5 h	68	273
					2) $[Pd_2(dba)_3]$ – $L^{22}Br$, 1,2-$Me_2C_6H_4$	–	274
	114	Br	Et		$[Pd_2(dba)_3]$ – $L^{114}Br$, 1,2-$Me_2C_6H_4$	–	274
	36a	Cl	Ph		$[\{Pd(\eta^2\text{-}2\text{-}Me_2NCH_2C_6H_4)(\mu\text{-}Cl)\}_2]$ [m] – $PBnPh_2$, $CHCl_3$ – AcOH, 20 °C, 4 days	21	205, 358
	36b	AcO	Ph		$Pd(OAc)_2$ – $PBnPh_2$, MeOH, 60 °C, 3 h	19	114, 358
	36c	Br	Ph		1) $[Pd(dba)_2]$ – $L^{36}Br$ (1 : 1), PhH, 20 °C, 1 h; 40 °C, 1 h; 70 °C, 0.5 h	79	273
					2) $[Pd_2(dba)_3]$ – $L^{36}Br$, 1,2-$Me_2C_6H_4$	–	274
	115a	AcO	Bn		–	–	358
	115b	Cl	Bn		–	–	358
	**37**	Cl	Bu^t	Bn	1) (*a*) Na_2PdCl_4 – PBu^tBn_2 (1 : 2), MeOH – PhH, 20 °C, 1 h; (*b*) AcONa (excess), MET, Δ, 24 h	30 [d] (35)	82
					2) (*a*) Na_2PdCl_4 – PBu^tBn_2 (1 : 2), MeOH – PhH, 20 °C,1 h; (*b*) Na_2PdCl_4 (1 equiv.), MET, Δ, 16 h; (*c*) AcONa (excess), MET, Δ, 25 h	13 [k] (15)	82
	78	Br	Ph	Me	$[Pd(dba)_2]$ – $L^{78}Br$ (1 : 1), PhH, 20 °C, 1 h; 40 °C, 1 h; 70 °C, 0.5 h	95	273
	116	AcO	Ph	Bn	$Pd(OAc)_2$ – HL^{116} (1 : 1.3), PhMe, 50 °C, 16 h	85	150, 358
	**65**		Ph	4,5-$(MeO)_2$	(*a*) $[PdCl_2(NCPh)_2]$ – HL^{65} (1 : 2), MeOH, 20 °C, 24 h; (*b*) AcONa (excess), MET, Δ, 2 h	83 [d] (91)	113
	66		Bu^t	4,5-$(MeO)_2$	(*a*) $[PdCl_2(NCPh)_2]$ – HL^{66} (1 : 2.1), EtOH, 20 °C, 15 h; (*b*) AcONa (excess), MET, Δ, 0.5 h	85 [d]	113
	77		Bu^t	4-F	Na_2PdCl_4 – HL^{77}	–	272
	**67**				$[PdCl_2(NCPh)_2]$ – HL^{67} (1 : 2.1), EtOH, 20 °C, 24 h, $CHCl_3$ – EtOH, 20 °C, > 42 days	10 [n]	113
	**39a**				$Pd(OAc)_2$ – P(1-Np)$_3$, PhMe, Δ	–	116
	39b		Me		$[Pd(acac)_2]$ – P(1-Np)$_3$, PhH, Δ	–	116
	**39c**		CF_3		$[Pd(hfac)_2]$ – P(1-Np)$_3$, PhH, Δ	–	116

Table 1 (continued).

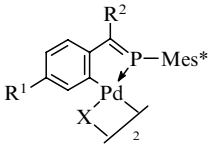
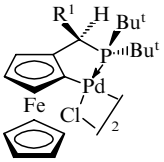
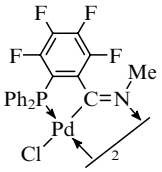
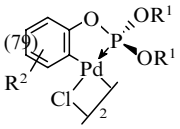
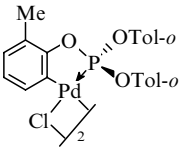
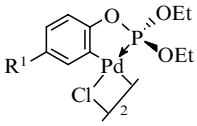
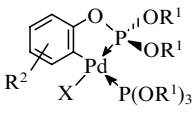
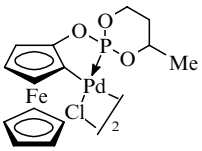
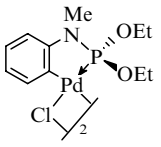
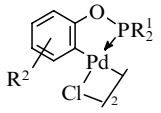
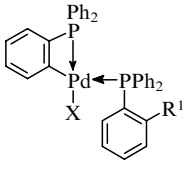
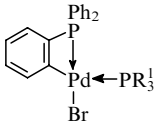
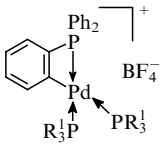
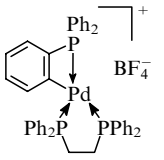
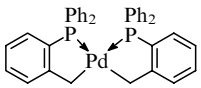
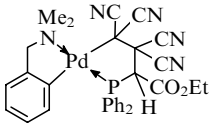
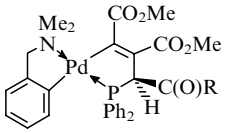
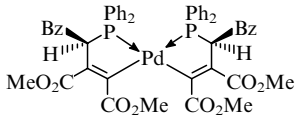
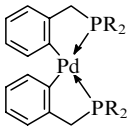
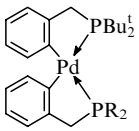
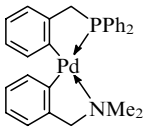
Complex [a]	Designation of the compound	X	R^1	R^2	Reagents and reaction conditions	Yield [b] (%)	Ref.
PC-Complexes with the $C(sp^2)-Pd$ bond							
	**40**	Cl	H	Ph	$[PdCl_2(NCMe)_2]$ [o] – HL^{40}, ÇHF, 20 °C, 5 h	97	117
	117 [c]	Cl	Bu[t]	Ph	$[PdCl_2(NCMe)_2]$ – HL^{117}, THF, 20 C, 5h	–	117
	118 [c]	Br	H	H	(*a*) $[Pd(dba)_2]$ – $L^{118}Br$, C_5H_{12}; (*b*) PhH, Δ, 1 h	–	323
	**52** [c]		H		(*a*) $Pd(OAc)_2$ – HL^{52} (1 : 1), PhMe, 20 °C, 8 h; (*b*) LiCl (2 equiv.), 20 °C, 2 h	70	132
	53		Me		(*a*) $Pd(OAc)_2$ – HL^{53} (1 : 1), PhMe, 20 °C, 1 h; (*b*) LiCl (5 equiv.), 20 °C, 20 min	93	131
	**99a** [c]				$[\{Pd(\mu\text{-}Cl)_2Pd(\mu\text{-}C(C_6F_5)=NMe)_2\}_n]$ – Ph_2PH, KOH (1 equiv.), Me_2CO	45	337
 (79)	**69a** 56		Ph	H	(*a*) $[PdCl_2(NCPh)_2]$ – $P(OPh)_3$ (1 : 2), CH_2Cl_2, 20 °C; (*b*) $PdCl_2$ (1 equiv.), PhMe, Δ, 5 h, N_2		76 [p, q]
	119a		*p*-Tol	5-Me	(*a*) $[PdCl_2(NCPh)_2]$ – $P(OTol\text{-}p)_3$ (1 : 2), CH_2Cl_2, 20 °C; (*b*) $PdCl_2$ (1 equiv.), PhMe, Δ, 5 h, N_2	80 [p, q] (100)	56
	120a		*m*-Tol	4-Me	(*a*) $[PdCl_2(NCPh)_2]$ – $P(OTol\text{-}m)_3$ (1 : 2), CH_2Cl_2, 20 °C; (*b*) $PdCl_2$ (1 equiv.), 1,4-$Me_2C_6H_4$, Δ, 1 h, N_2	71 [p, q] (79)	56
	60 [c]		2,4-$Bu^t_2C_6H_3$	3,5-Bu^t_2	$PdCl_2$ – HL^{60}	96	139
	**2a**				1) (*a*) $[PdCl_2(NCPh)_2]$ – $P(OTol\text{-}o)_3$ (1 : 2), CH_2Cl_2, 20 °C; (*b*) $PdCl_2$ (1 equiv.), PhMe, Δ, 5 h, N_2	70 [p, q] (80)	56
					2) (*a*) $PdCl_2$ – NaCl – $P(OTol\text{-}o)_3$ (1 : 2 : 2), EtOH, 20 °C, 2 h; (*b*) $PdCl_2$ – NaCl (1 : 1 : 2), EtOH, Δ, 1.5 h	see. [p] (60)	57
					3) (*a*) $[(\eta^5\text{-Cp})Pd(\eta^3\text{-}CH_2C(Cl)=CH_2)]$ – $P(OTol\text{-}o)_3$ (1 : 1), C_5H_{12}, 20 °C; (*b*) 80 °C, vacuum; (*c*) Al_2O_3, CH_2Cl_2 – C_5H_{12}; (*d*) CH_2Cl_2, HCl (gas)	14 [r] (90)	57
	**121**		MeO		(*a*) $[PdCl_2(NCPh)_2]$ – HL^{121} (1 : 2), CH_2Cl_2, 20 °C; (*b*) $PdCl_2$ (1 equiv.), 1,4-$Me_2C_6H_4$, Δ, 1 h, N_2	77 [p] (90)	56
	122		Me		(*a*) $[PdCl_2(NCPh)_2]$ – HL^{122} (1 : 2), CH_2Cl_2, 20 °C; (*b*) $PdCl_2$ (1 equiv.), 1,4-$Me_2C_6H_4$ Δ, 1 h, N_2	88 [p] (96)	56
	123		NO_2		(*a*) $[PdCl_2(NCPh)_2]$ – HL^{123} (1 : 2), CH_2Cl_2, 20 °C; (*b*) $PdCl_2$(1 equiv.), PhMe, Δ, 3 h, N_2	89 [p] (97)	56
	**69c**	Cl	Ph	H	(*a*) Na_2PdCl_4 – HL^{69} (1 : 2), EtOH, Δ, 0.5 min; 20 °C, 10 min; (*b*) decalin, Δ, 3 h	43 [p, q] (50)	143, 144
	119b	Cl	*p*-Tol	5-Me	(*a*) Na_2PdCl_4 – HL^{119} (1 : 2), EtOH, Δ, 0.5 min; 20 °C, 10 min; (*b*) decalin, Δ, 3 h	40 [p, q] (50)	143, 144
	120b	Cl	*m*-Tol	4-Me	(*a*) Na_2PdCl_4 – HL^{120} (1 : 2), EtOH, Δ, 0.5 min; 20 °C, 10 min; (*b*) decalin, Δ, 3 h	40 [p, q] (50)	143, 144
	124	Cl	4-ClC_6H_4	5-Cl	(*a*) $[PdCl_2(cod)]$ – HL^{124} (1 : 2), PhH, Δ, 0.5 min; 20 °C, 10 min; (*b*) decalin, Δ, 3 h	64 [p, q] (80)	143, 144
	2d	Cl	*o*-Tol	3-Me	(*a*) Na_2PdCl_4 – $P(OTol\text{-}o)_3$ (1 : 2), EtOH, Δ, 0.5 min; 20 °C, 10 min; (*b*) decalin, Δ, 3 h	40 [p, q] (50)	143, 144
	2e	Br	*o*-Tol	3-Me	(*a*) Na_2PdBr_4 – $P(OTol\text{-}o)_3$ (1 : 2), EtOH, Δ, 0.5 min; 20 °C, 10 min; (*b*) decalin, Δ, 3 h	15 [p, q] (20)	143, 144

Table 1 (continued).

Complex [a]	Designation of the compound	X	R^1	R^2	Reagents and reaction conditions	Yield [b] (%)	Ref.
	**125**				(*a*) $[PdCl_2(NCPh)_2]$ – HL^{125}, CH_2Cl_2, 20 °C, 15 min; (*b*) $PdCl_2$, K_2CO_3, PhMe (or PhH), Δ, 3 h	< 35 [p, s] (< 41)	140
	**126**				(*a*) $[PdCl_2(NCPh)_2]$ – HL^{126} (1 : 2), CH_2Cl_2, 20 °C; (*b*) $PdCl_2$ (1 equiv.), PhMe, Δ, 3 h, N_2	see [p]	56
	**58**		Ph	3,5-Bu^t_2	$PdCl_2$ – HL^{58}, PhMe, Δ, 18 – 20 h	52	138
	59		Pr^i	3,5-Bu^t_2	$PdCl_2$ – HL^{59}, PhMe, Δ, 18 – 20 h	50	138
	127		Ph	H	$[PdCl_2(NCPh)_2]$ – HL^{127}, THF, Δ, 20 h	65	138
	**80a** [c, t]	Br	Br		$[Pd(dba)_2]$ – 2-$BrC_6H_4PPh_2$ (1 : 2), PhMe, 20 °C, 45 min; Δ, 10 min	53	277, 278 [c]
	80b	Cl	H		$[PdCl_2(PPh_3)_2]$, DMF – H_2O, AcOLi	–	170
	80c [t]	Br	Cl		(*a*) $[Pd(dba)_2]$ – 2-$BrC_6H_4PPh_2$ (1 : 1), PhMe, 20 °C, 45 min; Δ, 10 min; (*b*) $PPh_2(C_6H_4Cl$-*o*) (4 equiv.), CH_2Cl_2, 20 °C, 15 days	44 [u] (60)	278
	80d [t]	Br	MeO		(*a*) $[Pd(dba)_2]$ – 2-$BrC_6H_4PPh_2$ (1 : 1), PhMe, 20 °C, 45 min; Δ, 10 min; (*b*) $PPh_2(C_6H_4OMe$-*o*) (4 equiv.), CH_2Cl_2, 20 °C, 48 h	63 [u] (86)	278
	**80e** [t]		Ph		(*a*) $[Pd(dba)_2]$ – 2-$BrC_6H_4PPh_2$ (1 : 1), PhMe, 20 °C, 45 min; Δ, min; (*b*) PPh_3 (4 equiv.), CH_2Cl_2, 20 °C, 30 min	62 [u] (85)	277
	80f [t]		Cy		(*a*) $[Pd(dba)_2]$ – 2-$BrC_6H_4PPh_2$ (1 : 1), PhMe, 20 °C, 45 min; Δ, 10 min; (*b*) PCy_3 (4 equiv.), CH_2Cl_2, 20 °C, 30 min	58 [u] (79)	277
	80g [t]		*p*-Tol		(*a*) $[Pd(dba)_2]$ – 2-$BrC_6H_4PPh_2$ (1 : 1), PhMe, 20 °C, 45 min; Δ, 10 min; (*b*) P(Tol-*p*)$_3$ (4 equiv.), CH_2Cl_2, 20 °C, 1 h	55 [u] (75)	278
	80h [t]		*m*-Tol		(*a*) $[Pd(dba)_2]$ – 2-$BrC_6H_4PPh_2$ (1 : 1), PhMe, 20 °C, 45 min; Δ, 10 min; (*b*) P(Tol-*m*)$_3$ (4 equiv.), CH_2Cl_2, 20 °C, 1 h	47 [u] (65)	278
	**80i**		Ph		(*a*) $[Pd(dba)_2]$ – 2-$BrC_6H_4PPh_2$ (1 : 1), PhMe, 20 °C, 45 min; Δ, 10 min; (*b*) $AgBF_4$ (4 equiv.), CH_2Cl_2 – THF, 20 °C, 5 h; *c*) PPh_3 (8 equiv.), 20 °C, 15 min	63 [u] (86)	278
	80j		*p*-Tol		(*a*) $[Pd(dba)_2]$ – 2-$BrC_6H_4PPh_2$ (1 : 1), PhMe, 20 °C, 45 min; Δ, 10 min; (*b*) $AgBF_4$ (4 equiv.), CH_2Cl_2 – THF, 20 °C, 5 h; (*c*) P(Tol-*p*)$_3$ (8 equiv.), 20 °C, 15 min	68 [u] (93)	278
	**80k**				(*a*) $[Pd(dba)_2]$ – 2-$BrC_6H_4PPh_2$ (1 : 1), PhMe, 20 °C, 45 min; Δ, 10 min; (*b*) $AgBF_4$ (4 equiv.), CH_2Cl_2 – THF, 20 °C, 5 h; (*c*) dppe (4 equiv.), 20 °C, 15 min	66 [u] (91)	278

[a] The structure of the primary cyclopalladation product is shown. [b] In the case of two- and three-stage syntheses, the overall yield is given, and the value in parentheses is the yield in the stage of closure of the PC-palladacycle. [c] The structure of the complex was confirmed by X-ray diffraction analysis. [d] Prepared by a two-stage route *via* a coordination intermediate of the *trans*-$[PdCl_2(HL^n)_2]$ type. [e] Prepared by a two-stage route *via* coordination intermediates of the *trans*-$[PdCl_2(HL^n)_2]$ and $[\{Pd(HL)Cl(\mu\text{-}Cl)\}_2]$ types without isolation of the latter. [f] Obtained by a two-stage route *via* binuclear coordination complex of the $[\{Pd(HL)Cl(\mu\text{-}Cl)\}_2]$ type. [g] Prepared *via* the intermediate complex $[Pd(hfac)_2(P(o\text{-}Tol)_3)]$ characterised by X-ray diffraction analysis.[196] [h] Two-stage synthesis through the intermediate [Pd(P⁀P)(Me)(H_2L^{71})]OTf complex, where P⁀P is ditertiary diphosphine. [i] Obtained by a two-stage route *via* the $[Pd^0(HL')_2]$ complex (HL′ = 2-$Ph_2PC_6H_4CH=CH_2$), whose structure was confirmed by X-ray diffraction.[34] [j] Binuclear complex **81b** is formed as a mixture with the mononuclear derivative of the same palladacycle with κ^1-bound diphosphine dippp. [k] Obtained by a three-stage route *via* two coordination intermediates, *trans*-$[PdCl_2(HL^n)_2]$ and $[\{Pd(HL)Cl(\mu\text{-}Cl)\}_2]$. [l] The reaction proceeds through a hydride intermediate, $[Pd(H)(X)(HL^{20})_2]$. [m] The starting complex was prepared by a known method.[357] [n] Isolated from a mixture with *trans*-$[PdCl_2(HL^{67})_2]$ by manual separation of the crystals. [o] The complex was characterised by X-ray diffraction analysis.[359] [p] Prepared by a two-stage route *via* the coordination intermediate *cis*-$[PdCl_2(HL^n)_2]$. [q] The synthesis of the intermediate coordination complex has been reported.[360] [r] Prepared by four-stage route *via* intermediate complexes, [η^5-CpPd(HL^2)(η^1-All′)], where All′ is $CH_2C(Cl)=CH_2$, [η^5-CpPdCl(HL^2)] and [η^5-CpPd(η^2-L^2)]. [s] A mixture of diastereomers. [t] A mixture of *cis* – *trans* isomers. [u] Prepared *via* the intermediate $[\{Pd(\mu\text{-}L^{80})_2Pd(\mu\text{-}Br)_2\}_2]$ complex whose synthesis has been reported.[277]

Table 2. Bis(chelate) spiro PC-complexes.

Complex [a]	Designation of the compound	R	Reagents and reaction conditions	Yield (%)	Ref.
	**84**		1) *trans*-$[Pd(PEt_3)_2Cl_2]$ – KL^{84} (~1 : 2), PhH, 20 °C, 1 h 2) *trans*-$[Pd(SEt_2)_2Cl_2]$ – KL^{84} (~1 : 2), PhH, 20 °C, 1 h	35 –	304, 305 304, 305
	**106b**		$[\{Pd(\eta^2\text{-}2\text{-}Me_2NCH_2C_6H_4)(\kappa^2\text{-}L')\}]$ [c] – $(NC)_2C{=}C(CN)_2$, THF, 20 °C; $(L')^-$ = $Ph_2PCH{=}C(OEt)O^-$	~100	345
	**103b**	Ph	$[Pd\{\eta^2\text{-}2\text{-}Me_2NCH_2C_6H_4)(\kappa^2\text{-}L')\}]$ [c] – $MeO_2CC{\equiv}CCO_2Me$ (1 : 1), CH_2Cl_2, 20 °C, 72 h; $(L')^-$ = $Ph_2PCH{=}C(Ph)O^-$	82	344
	105	OEt	$[Pd\{\eta^2\text{-}2\text{-}Me_2NCH_2C_6H_4)(\kappa^2\text{-}L')\}]$ [c] – $MeO_2CC{\equiv}CCO_2Me$ (1 : 1), THF, 20 °C; $(L')^-$ = $Ph_2PCH{=}C(OEt)O^-$	~100	345
	**103a** [b, d]		(*a*) *cis*-$[Pd(\kappa^2\text{-}L')_2]$ [c] – $MeO_2CC{\equiv}CCO_2Me$ (1 : 2), CH_2Cl_2, 20 °C, 36 h; (*b*) fractional crystallisation of a 3 : 1 mixture of diastereomers; $(L')^-$ = $Ph_2PCH{=}C(Ph)O^-$	66	343 [b], 344
	**36d** [e]	Ph	1) *trans*-$[PdCl_2(SEt_2)_2]$ – LiL^{36} (1 : 2), Et_2O, −20 to 20 °C, 2 h 2) *trans*-$[PdCl_2(SEt_2)_2]$ – LiL^{36} (1 : 2), PhH, 20 °C, 2 h	90 76	283 285
	83	Me	*trans*-$[PdCl_2(SEt_2)_2]$ – LiL^{83} (1 : 2), Et_2O, −20 to 20 °C, 2 h	70	283
	22c	Bu^t	*trans*-$[PdCl_2(SEt_2)_2]$ – LiL^{22} (1 : 2), Et_2O, −20 to 20 °C, 2 h	86	283
	**36e**	Ph	1) $[\{Pd(\eta^2\text{-}C_6H_4CH_2PBu^t_2\text{-}2)(\mu\text{-}Cl)\}_2]$ [f] – LiL^{36} [g] (1 : 2), PhH, 20 °C, 2 h 2) $[\{Pd(\eta^2\text{-}C_6H_4CH_2PBu^t_2\text{-}2)(\mu\text{-}Cl)\}_2]$ [f] – LiL^{36} [g] (1 : 2), Et_2O, −20 to 20 °C, 2 h	87 –	285, 301 283, 298
	83b	Me	$[\{Pd(\eta^2\text{-}C_6H_4CH_2PBu^t_2\text{-}2)(\mu\text{-}Cl)\}_2]$ [f] – LiL^{83} (1 : 2), Et_2O, −20 to 20 °C, 2 h	61	283, 298
	**36f** [b, e]		$[\{Pd(\eta^2\text{-}2\text{-}Me_2NCH_2C_6H_4)(\mu\text{-}Cl)\}_2]$ [h] – LiL^{36} (1 : 2), Et_2O, −20 to 20 °C, 2–3 h	89	284, 287, 361 [b]

[a] The structure of the primary cyclopalladation product is shown. [b] The complex was characterised by X-ray diffraction. [c] The synthesis of the starting complex has been reported.[346] [d] Complex *cis*-**103a** quantitatively isomerises into the *trans*-form upon thermolysis (THF, Δ, 12 h).[344] [e] A *cis*–*trans*-isomer mixture. [f] The starting complex was prepared by a known method.[82] [g] The synthesis of the LiL ligand has been reported.[301] [h] The synthesis of the starting complex has been reported.[357]

Table 3. PC-Chelating phosphine-substituted phosphorus ylides.

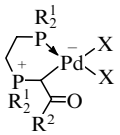
Complex [a]	Designation of the compound	X	R^1	R^2	Reagents and reaction conditions	Yield [b] (%)	Ref.
PC-Complexes with the $C(sp^3)-Pd$ bond							
	**86c** [c]	Cl	Ph	Ph	$PdCl_2(NCPh)_2$ – L^{86} (1 : 1), CH_2Cl_2, 20 °C	82	311 [c], 312 [c] 316, 317
	86d	Br	Ph	Ph	(*a*) $PdCl_2(NCPh)_2$ – $[HL^{86}]Br$ [d] (1 : 1), KOH, 18-C-6 (0.2 equiv.), CH_2Cl_2 – H_2O, 20 °C, 30 min; (*b*) NaBr, MeOH, 20 °C, 30 min	–	313
	128a	Cl	Ph	Me	$PdCl_2(NCPh)_2$ – L^{128} (1 : 1), CH_2Cl_2, 20 °C	56	315, 317
	129	Cl	Ph	MeO	$PdCl_2(NCPh)_2$ – L^{129} (1 : 1), CH_2Cl_2, 20 °C	85	315, 317
	130	Cl	Ph	EtO	$PdCl_2(NCPh)_2$ – L^{130} (1 : 1), CH_2Cl_2, 20 °C	85	315
	131	Cl	Bn	Ph	$PdCl_2(NCPh)_2$ – L^{131}	–	362

Table 3 (continued).

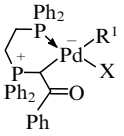
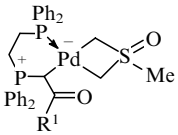
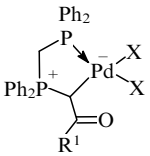
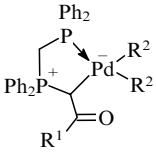
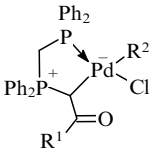
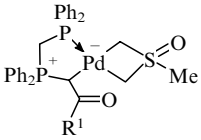
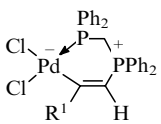
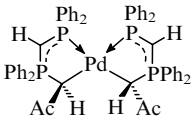
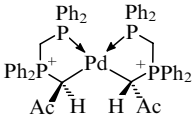
Complex [a]	Designation of the compound	X	R^1	R^2	Reagents and reaction conditions	Yield [b] (%)	Ref.
PC-Complexes with the $C(sp^3)-Pd$ bond							
	**86a** [e]	Cl	C_6Cl_5		$[\{R^1(THT)Pd(\mu\text{-}Cl)\}_2]-L^{86}$ (1 : 2), PhH, 20 °C, 30 min	69	318
	86b [e]	C_6F_5	C_6F_5		$[\{R^1_2Pd(\mu\text{-}Cl)\}_2]-L^{86}$ (1 : 2), Me_2CO, 20 °C, 30 min	57	318
	**86e**		Ph		(*a*) $[\{Pd(\eta^2(C,C)\text{-}(CH_2)_2S(O)Me)(\mu\text{-}I)\}_2]-[HL^{86}]Br$ (1 : 2), CH_2Cl_2, 20 °C; (*b*) 18-C-6 (0.2 equiv.), KOH, NaI, $CH_2Cl_2-H_2O$, 20 °C, 30 min	60	313
	128b		Me		(*a*) $[\{(\eta^2(C,C)\text{-}(CH_2)_2S(O)Me)Pd(\mu\text{-}I)\}_2]-[HL^{128}]Br$ (1 : 2), CH_2Cl_2, 20 °C; (*b*) 18-C-6 (0.2 equiv.), KOH, NaI, $CH_2Cl_2-H_2O$, 20 °C, 30 min	–	313
	**87a**	Br	Ph		1) (*a*) $[PdCl_2(NCPh)_2]-[HL^{87}]Br$ [d] (1 : 1), KOH, 18-C-6 (0.2 equiv.), $CH_2Cl_2-H_2O$, 20 °C, 30 min; (*b*) NaBr, MeOH, 20 °C, 30 min	65	313
					2) $Na_2PdCl_4-[HL^{87}]Br$ [d] (1 : 1), KOH, 18-C-6 (0.2 equiv.), $CH_2Cl_2-H_2O$, 20 °C	60	313
	87d	Cl	Ph		$[PdCl_2(NCPh)_2]-L^{87}$ (1 : 1), CH_2Cl_2, 20 °C	78	315, 317
	82c	Cl	Me		$[PdCl_2(NCPh)_2]-L^{82}$ (1 : 1), CH_2Cl_2, 20 °C	85	317
	82d	Br	Me		(*a*) $[PdCl_2(NCPh)_2]-[HL^{82}]Br$ [d] (1 : 1), KOH, 18-C-6 (0.2 equiv.), $CH_2Cl_2-H_2O$, 20 °C, 30 min; (*b*) NaBr, MeOH, 20 °C, 30 min	–	313
	85	Cl	MeO		$[PdCl_2(NCPh)_2]-L^{85}$ (1 : 1), CH_2Cl_2, 20 °C	80	317
	132a	Br	EtO		(*a*) $[PdCl_2(NCPh)_2]-[HL^{132}]Br$ [d] (1 : 1), KOH, 18-C-6 (0.2 equiv.), $CH_2Cl_2-H_2O$, 20 °C, 30 min; (*b*) NaBr, MeOH, 20 °C, 30 min	–	313
	**87e**		Ph	C_6F_5	$[Bu_4N]_2[\{R^2_2Pd(\mu\text{-}Cl)\}_2]-L^{87}$ (1 : 2), Me_2CO, 20 °C, 30 min	67	318
	82e		Me	C_6F_5	$[Bu_4N]_2[\{R^2_2Pd(\mu\text{-}Cl)\}_2]-L^{82}$ (1 : 2), Me_2CO, 20 °C, 30 min	70	318
	87f		Ph	C_6Cl_5	$[Bu_4N]_2[\{R^2_2Pd(\mu\text{-}Br)\}_2]-L^{87}$ (1 : 2), Me_2CO, 20 °C, 30 min	69	318
	82f		Me	C_6Cl_5	$[Bu_4N]_2[\{R^2_2Pd(\mu\text{-}Br)\}_2]-L^{82}$ (1 : 2), Me_2CO, 20 °C, 30 min	65	318
	**87g** [e]		Ph	C_6F_5	$[\{R^2(THT)Pd(\mu\text{-}Cl)\}_2]-L^{87}$ (1 : 2), PhH, 20 °C, 30 min	78	318
	82g [e]		Me	C_6F_5	$[\{R^2(THT)Pd(\mu\text{-}Cl)\}_2]-L^{82}$ (1 : 2), PhH, 20 °C, 30 min	76	318
	87h [e]		Ph	C_6Cl_5	$[\{R^2(THT)Pd(\mu\text{-}Cl)\}_2]-L^{87}$ (1 : 2), PhH, 20 °C, 30 min	81	318
	82h [e]		Me	C_6Cl_5	$[\{R^2(THT)Pd(\mu\text{-}Cl)\}_2]-L^{82}$ (1 : 2), PhH, 20 °C, 30 min	72	318
	**87c** [c]		Ph		(*a*) $[\{Pd(\eta^2(C,C)\text{-}(CH_2)_2S(O)Me)(\mu\text{-}I)\}_2]-[HL^{87}]Br$ (1 : 2), CH_2Cl_2, 20 °C; (*b*) 18-C-6 (0.2 equiv.), KOH, NaI, $CH_2Cl_2-H_2O$, 20 °C, 30 min	80	313
	82i		Me		(*a*) $[\{Pd(\eta^2(C,C)\text{-}(CH_2)_2S(O)Me)(\mu\text{-}I)\}_2]-[HL^{82}]Br$ (1 : 2), CH_2Cl_2, 20 °C; (*b*) 18-C-6 (0.2 equiv.), KOH, NaI, $CH_2Cl_2-H_2O$, 20 °C, 30 min	63	313
	132b		Et		(*a*) $[\{Pd(\eta^2(C,C)\text{-}(CH_2)_2S(O)Me)(\mu\text{-}I)\}_2]-[HL^{132}]Br$ (1 : 2), CH_2Cl_2, 20 °C; (*b*) 18-C-6 (0.2 equiv.), KOH, NaI, $CH_2Cl_2-H_2O$, 20 °C, 30 min	70	313
PC-Complexes with the $C(sp^2)-Pd$ bond							
	**101a** [c]		4-Me_2N-C_6H_4		$[Pd(dppm)Cl_2]$ [f] – 4-$Me_2NC_6H_4C\equiv CH$ (2 : 3), 1.4-dioxane – EDC, 105 °C, 72 h	31	339
	101b		Ph		$[Pd(dppm)Cl_2]$ [f] – $PhC\equiv CH$ (2 : 3), 1.4-dioxane – EDC, 110 °C, 90 h	49	339
	101c		4-NO_2-C_6H_4		$[Pd(dppm)Cl_2]$ [f] – 4-$NO_2C_6H_4C\equiv CH$ (1 : 1.1), 1.4-dioxane – EDC, 105 °C, 48 h	73	339
	101d		C_9H_{19}		$[Pd(dppm)Cl_2]$ [f] – $C_9H_{19}C\equiv CH$ (1 : 4), 1.4-dioxane – EDC, 110 °C, 100 h	48	339

Table 3 (continued).

Complex [a]	Designation of the compound	X	R^1	R^2	Reagents and reaction conditions	Yield [b] (%)	Ref.
Spiro PC-complexes with phosphino-phosphorus ylides							
	**82a** [c]				1) $Pd_2(dba)_3 \cdot CHCl_3 - HL^{82}$ (1 : 4), CH_2Cl_2, 20 °C, 10 min 2) $Pd(PPh_3)_4 - HL^{82}$ (1 : 2), CH_2Cl_2, 20 °C, 10 min 3) (*a*) $Pd(OAc)_2 - [H_2L^{82}]^+ ClO_4^-$ (1 : 2), CH_2Cl_2, 20 °C, 2 h; (*b*) NaH (excess), THF, 20 °C, 2 h $[H_2L^{82}]^+ = [Ph_2PCH_2P(Ph_2)CH_2Ac]^+$	66 67 –	282 282 282
	**82b**	ClO_4			1) $Pd_2(dba)_3 \cdot CHCl_3 - [H_2L^{82}]^+ ClO_4^-$ (1 : 8), CH_2Cl_2, 20 °C, 24 h 2) $Pd(OAc)_2 - [H_2L^{82}]^+ ClO_4^-$ (1 : 2), CH_2Cl_2, 20 °C, 2 h 3) (*a*) $Pd(PPh_3)_4 - HL^{82}$ (1 : 2), CH_2Cl_2, 20 °C, 10 min; (*b*) $HClO_4$(aq) (1 : 2), CH_2Cl_2, 20 °C, 1 h	53 73 43 (29)	282 282 282

[a] The structures of the primary products of closure of the phosphapalladacycle are shown. [b] In the case of two- and three-step syntheses, the total yield is given, while the yield in the stage of phosphapalladacycle closure is given in parentheses. [c] The structure of the complex was confirmed by X-ray diffraction analysis. [d] The synthesis of phosphonium salt has been reported.[315] [e] A mixture of *cis*–*trans* -isomers. [f] The synthesis of the starting complex has been reported.[340]

Table 4. Bicyclic PCP-structures.

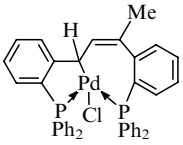
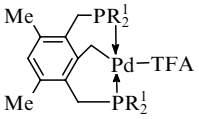
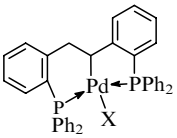
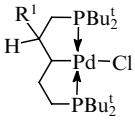
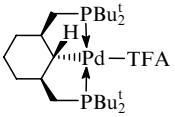
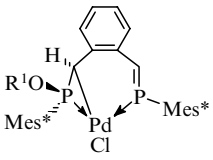
Complex [a]	Designation of the compound	X/Y	R^1	R^2 (*n*)	Reagents and reaction conditions	Yield [b] (%)	Ref.
PCP-Complexes with the $C(sp^3) - Pd$ bond							
	**19** [c]				$[PdCl_2(NCPh)_2] - HL^{18}$ (1 : 1), PhMe, MET, Δ, 2 h	70	68
	**11**			Pr^i	$Pd(TFA)_2 - HL^{11}$, THF, 80 °C	–	62
	12 [c]			Bu^t	$Pd(TFA)_2 - HL^{12}$, THF, 80 °C	–	62
	**27a**	Cl			$[PdCl_2(NCPh)_2] - HL^{27}$ (1 : 1), MET, Δ, 1.5 h	75	60, 61
	27b	Br			$K_2PdBr_4 - HL^{27}$ (1 : 1), MET, Δ, 2 h	26	60, 61
	27c	I			$[PdI_2(PPh_3)_2] - HL^{27}$ (1 : 1), MET, Δ, 10 h	86	60, 61
	**24a**	Cl	H		1) $[PdCl_2(NCPh)_2] - HL^{24}$ (1 : 1), EtOH, Δ, 18 h 2) (*a*) $[PdCl_2(NCPh)_2] - HL^{24}$ (1 : 1), EtOH, Δ, 18 h; (*b*) Δ, > 260 °C 3) (*a*) $[PdCl_2(NCPh)_2] - HL^{24}$ (1 : 1), EtOH, Δ, 18 h; (*b*) sublimation (260 °C, 0.01 atm)	12 [d] see [e] 40 [e] (64)	128 128 89, 157
	54 [c]	Cl	Me		$[PdCl_2(NCPh)_2] - HL^{54}$ (1 : 1), MET, Δ, 15 min	36	133
	**44**				$Pd(TFA)_2 - HL^{44}$ (1 : 1), THF, 80 °C, 1 h	91	91
	(*R*$_C$*R*$_P$)*-**95**	Me			(*a*) $[PdCl_2(NCPh)_2] - HL^{94}$ (1 : 1), CH_2Cl_2, 20 °C; (*b*) MeOH (excess), CH_2Cl_2, Δ, 24 h	~100 [f]	328
	(*R*$_C$*R*$_P$)*-**133** [c]	Et			(*a*) $[PdCl_2(NCPh)_2] - HL^{94}$ (1 : 1), CH_2Cl_2, 20 °C; (*b*) EtOH (excess), CH_2Cl_2, Δ, 5 days	~100 [f]	328

Table 4 (continued).

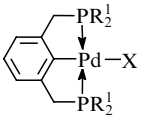
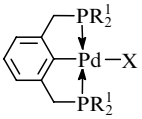
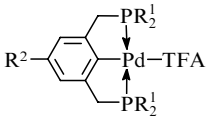
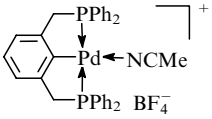
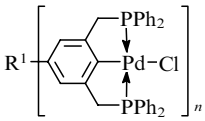
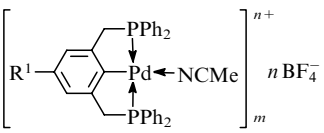
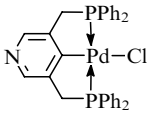
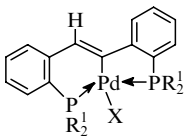
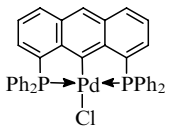
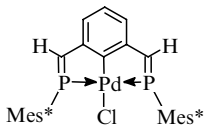
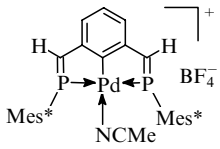
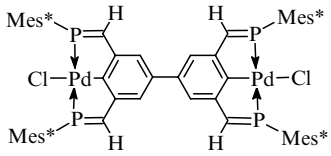
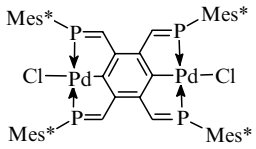
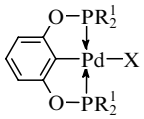
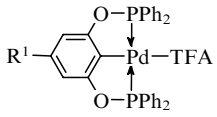
Complex [a]	Designation of the compound	X/Y	R^1	R^2 (*n*)	Reagents and reaction conditions	Yield [b] (%)	Ref.
PCP-Complexes with the C(sp^2)—Pd bond							
	**25a** [c]	Cl	Bu^t		$[PdCl_2(NCPh)_2]-HL^{25}$ (1 : 1) , MET, Δ, 25 min	75	90, 363 [c]
	25b	TFA	Bu^t		1) $Pd(TFA)_2-HL^{25}$ (1 : 1), PhMe, 130 °C, 1 h (in a sealed tube)	~ 100	151
	**25b**	TFA	Bu^t		2) $Pd(TFA)_2-L^{25}OEt$ (1 : 1), PhMe, 130 °C, 3 h (in a sealed tube)	< 10 [g]	151
					3) (*a*) $Pd(TFA)_2-L^{25}OMe$ (1 : 1), C_6D_6, 85 °C, 3 h (in a sealed tube); (*b*) PhMe, 30 atm of H_2, 180 °C, 8 h	~ 55 [h] (~ 55)	151
	17a [c]	Cl	Ph		1) $[PdCl_2(NCMe)_2]-HL^{17}$ (1 : 1), CH_2Cl_2, 20 °C, 10 min	75	66, 364 [c]
					2) $[PdCl_2(NCMe)_2]-HL^{17}$, MET, 150 °C	—	120
	62a [c]	Br	Cy		*trans*-$[PdBr_2(PPh_3)_2]-HL^{62}$ (1 : 2), EtOH, Δ, 16 h	72	155
	62b [c]	Cl	Cy		1) $[PdCl_2(NCPh)_2]-HL^{62}$ (1 : 1.3), MET, Δ, 25 min	17 [i]	155
					2) (*a*) $[PdCl_2(NCPh)_2]-HL^{62}$ (1 : 1.3), MET, Δ, 25 min; (*b*) MET, Δ, 48 h	31 [j] (43)	155
	134	Cl	4-Me_2N-C_6H_4		$[PdCl_2(NCPh)_2]-HL^{134}$ (1 : 1.1), CH_2Cl_2, 120 °C, 12 h (autoclave)	63	120
	135	TFA	Pr^i		$Pd(TFA)_2-HL^{135}$, THF, 80 °C	—	62
	136	TFA	cyclo-C_5H_9		(*a*) $HL^{136}\cdot 2\,BH_3$, morpholine, 120 °C, 2 h; (*b*) $Pd(TFA)_2$, THF, 70 °C	75 [k]	152
	**109**		Bu^t	Me	(*a*) $Pd(TFA)_2-L^{109}OH$ (1 : 1), PhMe, 20 °C, 12 h; (*b*) PhMe, 30 atm of H_2, 180 °C, 8 h	~ 55 [l] (~ 55)	151
	137		cyclo-C_5H_9	BnO	(*a*) $HL^{137}\cdot 2\,BH_3$, morpholine, 120 °C, 2 h; (*b*) $Pd(TFA)_2$, THF, 70 °C	55 [k]	152
	**17b**				$[Pd(NCMe)_4](BF_4)_2-HL^{17}$ (1 : 1), THF–MeCN, 50 °C, 30 min	42	164
	**138a**		C≡C	(2)	(*a*) $[Pd(NCMe)_4](BF_4)_2-H_2L^{138}$ (2 : 1), MeCN, Δ, 2 h; (*b*) NaCl (excess), $CH_2Cl_2-H_2O$, 20 °C, 12 h	50 (51)	50
	139a		$(C\equiv C)_2$	(2)	(*a*) $[Pd(NCMe)_4](BF_4)_2-H_2L^{139}$ (2 : 1), MeCN, Δ, 1 h; (*b*) NaCl (excess), $CH_2Cl_2-H_2O$, 20 °C, 12 h	20 (21)	50
	140a		1,3,5-$(C\equiv C)_3$. .C_6H_3	(3)	(*a*) $PdCl_2-AgBF_4$ (1 : 2), MeCN, Δ, 5 min (*in situ*); (*b*) H_3L^{140} (0.33 equiv.), CH_2Cl_2, Δ, 1 h; (*c*) NaCl (excess), $CH_2Cl_2-H_2O$, 20 °C, 3 h	88 (90)	49
	141		1,3,5-$(OCH_2)_3C_6H_3$	(3)	(*a*) $[Pd(NCMe)_4](BF_4)_2-H_3L^{141}$ (3 : 1) , MeCN, 20 °C, 15 min; (*b*) NaCl (excess), $CH_2Cl_2-H_2O$, 20 °C,12 h	67	48
	142		1,3-$(OCH_2)_2$. .$C_6H_3CH_2CN$-5	(2)	(*a*) $[Pd(NCMe)_4](BF_4)_2-H_2L^{142}$ (2 : 1), MeCN, 20 °C, 15 min; (*b*) NaCl (excess), $CH_2Cl_2-H_2O$, 20 °C, 12 h	55	48
	**138b** [c]		C≡C	(2)	$[Pd(NCMe)_4](BF_4)_2-H_2L^{138}$ (2 : 1) , MeCN, Δ, 2 h	51	50
	139b		$(C\equiv C)_2$	(2)	$[Pd(NCMe)_4](BF_4)_2-H_2L^{139}$ (2 : 1), MeCN, Δ, 1 h	21	50
	140b		1,3,5-$(C\equiv C)_3C_6H_3$	(3)	(*a*) $PdCl_2-AgBF_4$ (1 : 2), MeCN, Δ, 5 min (*in situ*); (*b*) H_3L^{140} (0.33 equiv.), CH_2Cl_2, Δ, 1 h	90	49
	**68b**				(*a*) $[PdCl_2(NCPh)_2]-HL^{68}$ (1 : 1), CH_2Cl_2, 100 °C, 12 h (autoclave); (*b*) Et_3N, PhMe–H_2O	(63) [m]	168

Table 4 (continued).

Complex [a]	Designation of the compound	X/Y	R^1	R^2 (*n*)	Reagents and reaction conditions	Yield [b] (%)	Ref.
PCP-Complexes with the C(sp^2) – Pd bond							
	**10a**	Cl	Ph		$[PdCl_2(NCPh)_2]$ – HL^{10} (1 : 1), PhH, Δ, 1 h	72	60, 61
	10b	Br	Ph		K_2PdBr_4 – HL^{10} (1 : 1), MET, Δ, 2 h	79	60, 61
	45a	Cl	*o*-Tol		$[PdCl_2(NCPh)_2]$ – HL^{45} (1 : 1), PhH, Δ, 16 h	62	60, 61
	45b	Br	*o*-Tol		K_2PdBr_4 – HL^{45} (1 : 1), 1,3,5-$Me_3C_6H_3$, Δ, 24 h	67	60, 61
	45c	I	*o*-Tol		$PdCl_2$ – NaI – HL^{45} (1 : 13 : 1), MET, Δ, 96 h	50	60, 61
	**73** [c]				$[PdCl_2(NCPh)_2]$ – HL^{73} (1 : 1), MET, Δ, 2h	73	156
	**63a** [c]				$[PdCl_2(NCPh)_2]$ – HL^{63} (1 : 1), CH_2Cl_2, 20 °C, 2 h	–	125, [c] 127
	**63b**				$[Pd(NCMe)_4](BF_4)_2$ – HL^{63} (see [n]) (1 : 1), CH_2Cl_2, 20 °C, 2 h	–	127
	**64** [c]				$[PdCl_2(NCPh)_2]$ – H_2L^{64} (1 : 1), CH_2Cl_2 , 20 °C, 0.5 h	90	126
	**49**				(*a*) $[PdCl_2(NCMe)_2]$ – H_2L^{49} (2 : 1), THF, 20 °C, 0.5 h; (*b*) THF, 20° C, 4 h	(60) [o]	117
	**79** [c]	I	4-$MeOC_6H_4O$		(*a*) 2,6-$(HO)_2C_6H_3I$ – $(4\text{-}MeOC_6H_4O)_2PNEt_2$ – tetrazole (1 : 3 : 6), THF, −78 to 20 °C, 2 days (*b*) $Pd_2(dba)_3 \cdot CHCl_3$ (0.5 equiv.), PhMe, 23 °C, 12h	(26)	275
	48 [c]	Cl	Pr^i		$PdCl_2(cod)$ – HL^{48} (1 : 1), PhMe, Δ, 5 h	90 – 95	122, [c] 158
	**46** [c]		H		$Pd(TFA)_2$ – HL^{46} (1 : 1), THF, 20 °C, 2 h	85	121
	47		Me		$Pd(TFA)_2$ – HL^{47} (1 : 1), THF, 20 °C, 2 h	78	121

[a] The structure of the primary cyclopalladation product is shown. [b] In the case of two- and three-step syntheses, the total yield is given, while the yield in the stage of phosphapalladacycle closure is given in parentheses. [c] The structure of the complex was confirmed by X-ray diffraction analysis. [d] The major reaction product (62%) is the macrocyclic coordination complex, $[Cl_2Pd(\mu{:}\kappa^2\text{-}HL^{24})_2PdCl_2]$. [e] Prepared *via* the $[Cl_2Pd(\mu\text{-}HL^{24})_2PdCl_2]$ coordination complex whose synthesis has been reported.[128] [f] Prepared *via* the intermediate $[Pd(\kappa^2\text{-}L^{94})Cl_2]$ complex, where $L^{94} = C_6H_4(CH{=}PMes^*)_2$-1,2, whose structure has been confirmed by X-ray diffraction analysis.[328] [g] The product is formed as a mixture with $[(\kappa^3\text{-}L^{25}O)Pd(TFA)]$ (1 : 9 ratio), which was characterised by X-ray diffraction.[151] [h] Prepared through the intermediate $[(\kappa^3\text{-}L^{25}O)Pd(TFA)]$ complex, whose synthesis has been reported.[347] [i] The major reaction product (71%) is the dimeric $[Cl_2Pd(\mu{:}\kappa^2\text{-}HL^{62})_2PdCl_2]$ complex. [j] Prepared in two stages *via* the intermediate $[\{Cl_2Pd(\mu\text{-}HL)\}_2]$ coordination complex. [k] The yield is given over two stages including the removal of ligand protection. [l] Prepared in two stages *via* the intermediate $[(\kappa^3\text{-}L^{109}O)Pd(TFA)]$ complex. [m] The complex was obtained *via* the PCP-intermediate $[(\eta^3\text{-}L^{68}H)PdCl]^+Cl^-$. [n] The ligand structure was confirmed by X-ray diffraction analysis. [o] The complex was obtained through the $[(PdCl_2)_2(\mu{:}\ \kappa^2,\kappa^2\text{-}H_2L^{49})]$ intermediate.

VIII. Conclusion

Despite the diversity of the known structural types of phosphapalladacycles and routes for their synthesis, the topicality of further development of the chemistry of this highly interesting and practically valuable class of organometallic compounds is beyond doubt.

Among the preparative aspects of this field of chemistry, development of the processes based on the use of highly reactive organometallic reagents for direct intramolecular activation of the C – H bonds of P-donor ligands seems to be most fruitful. For

example, η^3-allylic palladium complexes have been barely used for this purpose as yet, and examples of using other metallating agents with the Pd–C bond are sparse. From the structural standpoint, of interest are the synthesis and evaluation of properties and reactivity of CPC-, CPP- and CPN-type bicyclic complexes and diverse tricyclic compounds with phosphapalladacyclic fragments.

Apparently, further development of the chemistry of phosphapalladacycles would not be limited to the extention of the collection of mono- and bicyclic complexes of this class. Highly topical is detailed investigation into the mechanisms of direct intramolecular activation of the C–H-bonds in P-donor ligands, which would enable more purposeful construction of new structures of this class.

* * *

As the manuscript was being prepared for publication, a number of studies appeared that cover to some extent the 'blank spots' mentioned above. A significant contribution to the development of this domain of chemistry has been made by the synthesis of a number of cyclopalladated derivatives of P-donor ligands of new structural types. The first PCP-complex with two fused six-membered metallacycles with a palladated sp^2-hybridised carbon atom has been prepared by oxidative addition of the bromo-substituted diphosphine $2,6\text{-}(Ph_2PCH_2CH_2)_2C_6H_3Br$ to $Pd(dba)_2$.[365] The earlier attempts to produce such a structure by direct activation of the C–H bond failed.[67] Methods of synthesis of new non-symmetrical tricyclic PCP-[366,367] and PCN-type structures,[368,369] differing in the sizes of two metallacycles (five- and six-membered [366–369]) and/or the nature of two heterodonor centres (with a phosphino [367] or amino group [368,369] in combination with a phosphinite branch) from mono- and bis(phosphinites) have been developed. Previously, only three asymmetrical PCP-complexes with phosphine donor groups were known.[60,61,68]

In addition to the known PC-complexes with a six-membered metallacycle (based on the exotic sydnonylphosphine ligand [63]), two other representatives of this class have been synthesised from (2-diphenylphosphinophenyl)ferrocene [370] and 2-(dicyclohexylphosphino)biphenyl.[371] Double cyclopalladation of the same aromatic ring of 2-methylresorcinolbis(phosphinite) was implemented for the first time.[372] The collection of monocyclic cyclopalladated phosphite [373–375] and phosphinite [376] derivatives with five-membered PC-palladacycles has been substantially extended. Most of the new PC- and PCP-complexes have been obtained by direct activation of the C–H bonds in the corresponding ligands on treatment with $PdCl_2$,[374–376] $[PdCl_2(cod)]$,[366,367] $[PdCl_2(NCR)_2]$,[373,376] $Pd(OAc)_2$ [370,371] or $Pd(TFA)_2$,[372] the product yields ranging from moderate (43%–48% [367,375]) to nearly quantitative (92%–94% [370,371]). A new approach based on chloropalladation of alkynes bearing heterodonor substituents has been developed for the preparation of asymmetrical pincer PCN-structures.[368,369] An interesting way of generating PCC-complexes from bis(phosphonium) salts (precursors of P-ylides) has been developed only for platinum(II): the process formally includes the activation of three C–H and one C–P bond.[377]

The vast majority of new complexes have been synthesised with the aim of being tested as (pre)catalysts. The presence of persisting interest in this line of practical use of phosphapalladacycles is indicated by the multitude of new reviews [378–383] devoted to this topic. For solving the problem of regeneration of cyclopalladated catalysts, methods of fixing of one of the PCP-complexes on silica gel have been developed, in particular, by direct activation of the C–H bond of the pre-immobilised diphosphine ligand under the action of $Pd(TFA)_2$.[384]

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