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Phosphapalladacycles: forms of existence and reactions †

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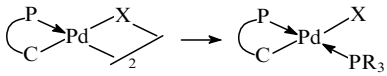
Abstract. Some aspects of the reactivity of cyclopalladated complexes with phosphorus donor atoms are discussed, in particular, the routes of modification of the metal coordination environment in phosphapalladacycles by means of diverse auxiliary ligands; the transformations of phosphapalladacycles involving the Pd – C bond; the modification of phosphapalladacycles with retention of the Pd – C bond; and dechelation and destruction of phosphapalladacycles. The regiochemistry of ligand coordination to PC-palladacycles is considered from the standpoint of the *trans*-effect of the P- and C-donor atoms of the palladacycle. The bibliography includes 359 references.

I. Introduction

The development of modern chemistry of phosphapalladacycles is mainly determined by the increased demands of the homogeneous metal complex catalysis for compounds of this class, as they proved to be remarkably efficient and practically convenient catalysts or precatalysts.[1 – 11] There are two approaches to the optimisation of the structures of phosphapalladacycles to meet the requirements of a particular chemical process and a particular substrate: (1) modification of electronic and steric characteristics of the phosphapalladacycle and (2) variation of the nature of auxiliary ligands in the coordination environment of palladium.

The first approach (usually, fairly labour consuming) involves targeted design of P-donor ligands and the selection of optimal methods for their cyclopalladation. The relevant information can be found in a review,[12] which gives a detailed analysis of the known methods for the synthesis of the PC- and PCP-type cyclopalladated complexes (CPCs). An alternative solution to this problem is chemical modification of the phosphapalladacycle prepared beforehand. The influence of the structure of phosphapalladacycles on their catalytic activity can be followed from a series of reviews on homogeneous catalysis, which are devoted to either particular types of reactions [2, 3, 6, 13] or particular classes of cyclopalladated (pre)catalysts of the PC [5, 7, 8] or PCP type.[4, 5, 7, 9 – 11]

The second approach appears less labour consuming, as it implies only the variation of the coordination environment of the metal in the pre-formed phosphapalladacycles. Its efficiency can be illustrated by the substantial increase in the activity of the PC-type (pre)catalysts in the Suzuki and Stille reactions and in amination attained on passing from standard dimeric complexes to monomeric analogues (mononuclear palladium complexes) with monodentate phosphines.[14 – 18]



Conversely, in other processes (for example, in the Heck reaction), the activity of the monomeric phosphine derivatives proved to be lower than the activity of the dimers.[19, 20] The activity of the cyclopalladated catalysts can be substantially enhanced by selecting an appropriate bridging anion in the CPC dimers ($Cl^- < AcO^- < CF_3COO^-$) [21] or by converting dimers into monomeric β-diketonate derivatives.[22] Similar effects have been found for the use of CN-palladacycles whose catalytic activity in various processes can either increase [23 – 28] or, conversely, decrease [29] on passing from dimers to monomers. For example, the cationic mononuclear adducts of the CN-palladacycles efficiently catalyse CO copolymerisation with ethylene,[30] while in the Heck reaction they show no activity.[29] These facts demonstrate the necessity of individual approach to the coordination environment of palladium in the palladacycle chosen for catalysis.

The implementation of the second approach requires the knowledge of synthetic routes to various derivatives of a palladacycle and of their behaviour in chemical transformations. The only published review on the cyclometallation of phosphorus-containing ligands (separately [31] and in the monograph [32]) covers the literature only up to 1985 and does not describe the behaviour of phosphapalladacycles in various reactions or the modification routes of the coordination environment of palladium.

The purpose of this review is to analyse the properties and the reactivity of phosphapalladacyclic compounds based on publica-

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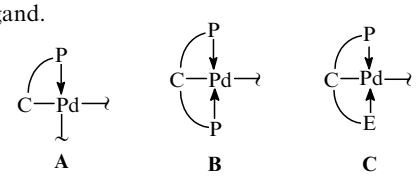
† This review naturally continues the review by the same authors 'Phosphapalladacycles: preparation routes' published previously [*Russ. Chem. Rev.* **73** 309 (2004)].

tions that appeared up to 2003. Two different types of reactions are considered:

1. Modification of the coordination environment of the metal in phosphapalladacycles by introducing auxiliary ligands without affecting the proper metallacyclic fragment (Section II).

2. Transformations of phosphapalladacycles (Section III): reactions involving the Pd–C bond and processes resulting in palladacycle modification with retention of the cyclic structure. This Section also covers dechelation and destruction of palladacycles.

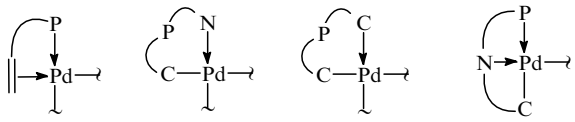
The investigation objects include mono- (**A**) and bicyclic (**B**, **C**) compounds in which palladium is directly linked to one or two atoms of trivalent phosphorus and to, at least, one carbanionic centre incorporated in the same anionic bi- or tridentate chelated ligand.



A **B** **C**

E is heteroatom.

The structures of type **D**–**G**



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

are beyond the scope of this review as their properties differ significantly from the properties of phosphapalladacycles **A**–**C**.‡

However, PC-chelated derivatives of phosphino-phosphorus ylides are included in the consideration, despite the formally neutral nature of ligands of this class (really, the zwitterionic nature), because the C-donor atom in them exhibits pronounced carbanion properties.

An idea of the diversity of derivatives possible for CPC bearig P-donor atoms can be gained from Supplements 1–3, which present data on the methods of synthesis of phosphapalladacycle derivatives classified according to structural features: PC-type compounds (**A**, Supplement 1), their bicyclic (pincer) PCP-analogues (**B**, Supplement 3) and PC-coordinated phosphino-phosphorus ylides (Supplement 2). Within each Table, phosphapalladacycles are grouped according to the type of hybridisation of the metal-bonded carbon atom (sp^3 or sp^2) and the size of the chelate ring (six-, five-, four-, and three-membered). In addition, derivatives of each palladacycle are classified according to types of complexes, either neutral or cationic, with either mono- or bidentate auxiliary ligands. The complexes whose structures were reliably confirmed by X-ray diffraction are asterisked.

II. Forms of existence of phosphapalladacycles

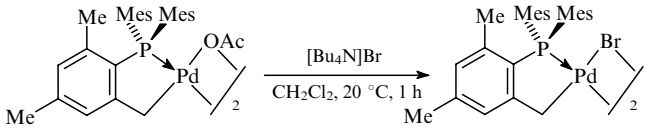
This Section describes phosphapalladacycle derivatives of PC- and PCP types and their interconversion routes.

1. Monocyclic PC-complexes

a. Dimers

The direct intramolecular cyclopalladation of monodentate P-donor ligands usually gives, as the primary products, dimeric complexes with halide or carboxylate bridges, most often, chloride or acetate ones (depending on the nature of the palladating agent used).[12] Modification of bridged anions is required in those cases where it is necessary (1) to increase the dimer solubility (most often, the solubility of μ-halide dimers is lower than that of μ-carboxylate analogues); (2) to remove the complications caused by the dynamic behaviour of complexes (most typical of μ-carboxylate dimers[2,22,51]); (3) to increase the thermal stability of complexes;§ (4) to optimise the structure of a dimeric PC-type (pre)catalyst.[21]

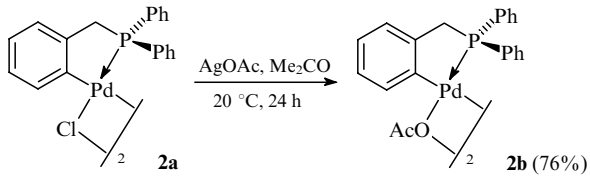
The transformation of μ-acetate PC-dimers into μ-chloride or μ-bromide analogues is easily accomplished by simple replacement of μ-OAc by a 'softer' halide at room temperature (see Supplement 1). The reactions with LiCl are carried out in a mixture of methanol with dichloromethane[53] or in aqueous acetone,[54] while those with ammonium salts (for example, with $[Bu_4N]Cl$ or $[Bu_4N]Br$) are carried out in dichloromethane. An example of anion exchange in dimer **1a** is presented below¶ (see Ref. 51).



1a **1b** (86%)

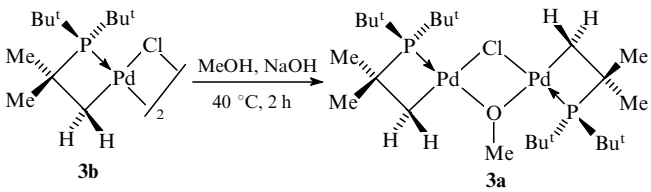
The μ-chloride PC-dimers are usually transformed into μ-bromide or μ-iodide analogues (with softer anions) by means of simple metal halide salts KBr,[55,56] LiBr,[57] KI[55,57] and NaI.[58,59] The reactions are carried out in acetone at room temperature.

However, the reverse replacement of relatively soft bridging halide anions in dimers by harder anions (for example, the **2a** → **2b** transition) requires dehalogenation of the substrate with an appropriate RCO_2Ag salt (R = Me, Ph).[54,60]



2a **2b** (76%)

Of the few non-standard forms of dimeric CPC with monoatomic bridges, we would like to mention the non-symmetrical μ-methoxy-μ-chloride complex **3a**, which is prepared by methoxylation of μ-chloride dimer **3b** with methanol in an alkaline medium.[61]



3b **3a**

As was to be expected, the reaction of non-symmetrical dimer **3a** with phosphine affords a mixture of two mononuclear derivatives with different anions.

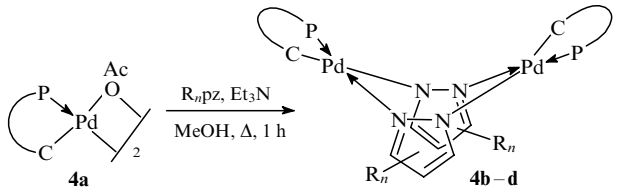
One more type of dimeric CPCs with diatomic bridges includes phosphapalladacycles with azolate bridges, namely, pyrazolate (pz),[62–64] 4-methyl- (4-mpz) and 3,5-dimethyl-substituted (3,5-dmpz) pyrazolate bridges.[63,64] These binuclear com-

‡ Examples of structures **D**–**G** have been reported.[33–50]

§ For PC-palladacycles, these studies have not been carried out, but the stability of benzylaminate CN-dimers is known[52] to increase, depending on the nature of the bridging anions, in the series $CN^- < NCO^- < Cl^- < SCN^-$.

¶ In the designations of complexes, the Arabic numeral corresponds to the superscript in the designation of the cyclopalladated ligand HL^n, while the letters are used to number particular derivatives of a particular phosphapalladacycle (see the designations in the previous review[12]).

plexes are prepared by treatment of the μ-acetate [63, 64] or μ-chloride [62] dimer with pyrazole. In the former case, the reaction is carried out in the presence of Et_3N in methanol on heating, while in the latter case, in the presence of NaOH at room temperature. In both cases, the yields are relatively high (80% – 97%). The scheme of transformation of dimer **4a** into pyrazolate analogues **4b** – **d** is shown below.

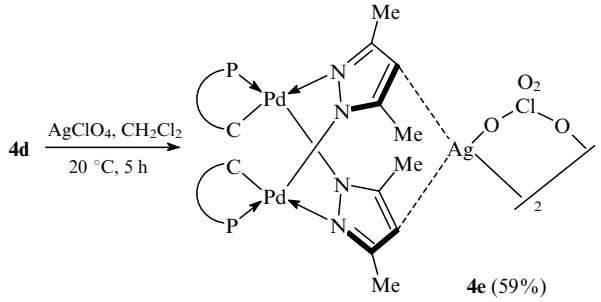


P C = *o*-$CH_2C_6H_4P(Tol\text{-}o)_2$ (L^4);

R_n = H (**4b**, 91%), 4-Me (**4c**, 87%), 3,5-Me_2 (**4d**, 97%).

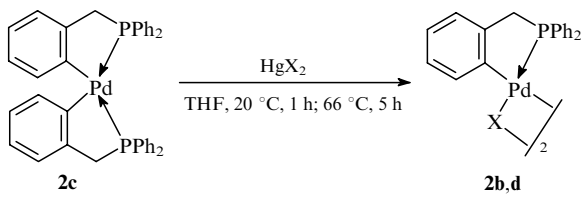
In the μ-pyrazolate dimers, the central six-membered ring $\{Pd_2N_4\}$ involves two nitrogen atoms from each bridging ligand. This determines the structural diversity of dimers **4b** – **d**. Since the tetraazadipalladacycle exists as the boat conformation, the complexes acquire the shape of a 'half-open book' (a typical shape of μ-carboxylate dimers). The same conformation is typical of simple coordination compounds of palladium with bridging pyrazolate ligands.[65, 66]

With this orientation of two flat pyrazolate ligands, a π-electron-enriched gap convenient for incorporation of a cation of another metal is formed between them. The reaction of bridging 3,5-dimethylpyrazolate ligands in dimer **4d** with $AgClO_4$ provides an example of secondary complexation.[63, 64]



The structure of hexanuclear complex **4e** was confirmed by X-ray diffraction analysis.[63] The structural parameters of this complex were interpreted as being indicative of η^1-binding of the silver ion to the unsubstituted carbon atoms of the two bridging pyrazolate ligands, which are arranged at a 44.8° angle with respect to each other.

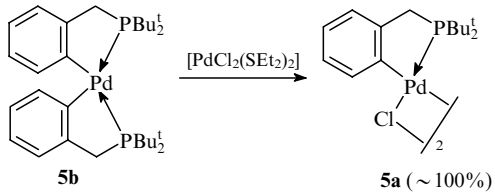
The synthesis of dimeric CPCs from *spiro*-complexes is important from the practical standpoint. The easy cleavage of the bridges, which allows one to modify the coordination environment of the metal by introducing auxiliary ligands (see Section II.1.b) is a valuable advantage of dimers with bridging anions compared to *spiro*-PC-structures. The *spiro*-complex can be converted into the dimer in two ways: on treatment with mercury(II) bromide or acetate or on treatment with an appropriate palladium(II) halide.[67]



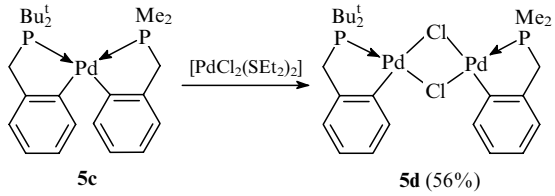
X = AcO (**2b**, 77%), Br (**2d**, 86%).

The drawbacks of the former method include the formation of mercury metal in the reaction and the requirement to strictly maintain the 1 : 1 reactant ratio, as an excess of a mercury salt (for example, $HgBr_2$) promotes full cleavage of the Pd – C bond to give a coordination complex of palladium(II) bromide with *ortho*-mercurated phosphine [67] (see Section III.3.a).

The latter method based on the use of a stoichiometric amount of the $[PdCl_2(SEt_2)_2]$ complex is more convenient and usually gives binuclear μ-halide compounds in high yields. For example, μ-chloride dimer **5a** was synthesised from *spiro*-complex **5b** in a quantitative yield.[67]



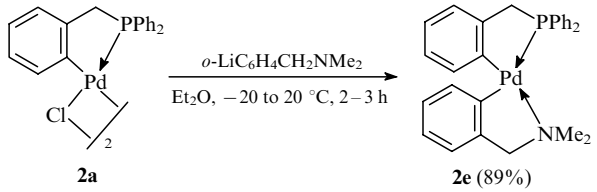
At first glance, it seems attractive to prepare μ-chloride dimers by this method using two different phosphapalladacycles. An attempt to implement this idea has been reported.[67]



However, due to the relatively low yield of product **5d** and the known dynamic behaviour of dimeric complexes,[51, 68, 69] which opens the way for easy migration of palladacycles between mixed-ligand dimer molecules, one can hardly expect reactions of this type to be selective.

Polymeric palladium chloride can also be used for this purpose instead of $[PdCl_2(SEt_2)_2]$, but this is less efficient and requires more drastic conditions (refluxing in xylene for many hours). In addition, the process can be complicated by the side formation of the palladium(II) complex with *ortho*-chlorinated phosphine.[67] The possibility of using hydrogen chloride in ether for converting the *spiro*-complex into the corresponding μ-chloride dimer was shown for the platinum analogues. Under these conditions, the formation of the $[\{Pt(\eta^2\text{-}L^5)(\mu\text{-}Cl)\}_2]$ dimer from the mononuclear *cis*-$[Pt(\eta^2\text{-}L^5)_2]$ complex has been detected by spectroscopy.[70]

The transformation of μ-halide dimers into *spiro*-complexes is possible only when *ortho*-lithiated derivatives, for example, *o*-$LiC_6H_4CH_2XR_2$ (X = N, P, As; R = Alk, Ar) (see Supplement 1), are used as auxiliary ligands.[71 – 73] The reactions of this type proceed under mild conditions (Et_2O, – 20 °C) usually giving the corresponding *spiro*-complexes in high yields (61% – 89%). This method allows the preparation of mixed-ligand (heteroleptic) complexes including those with different heterodonor atoms in two palladacycles (for example, complex **2e**).



Note that other routes for the transformation of μ-halide dimers into *spiro*-complexes are also known in the chemistry of the CN analogues. For example, one can use organotin derivatives of

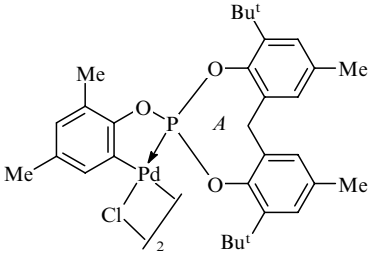
the incoming ligand.[74,75] This type of transformation has been observed during the CPC carbonylation.[76] Using cycloplatinated complexes as examples, it was demonstrated that a non-functionalised ligand (azobenzene) can be involved in this process with assistance by silver ions.[77] However, it remains obscure whether these methods can be adapted to PC-systems.

μ-Halide dimeric CPCs usually exist as mixtures of geometric isomers (*syn*- and *anti*-isomers). When the molecule contains stereocentres or other chirality elements, the number of isomers increases to at least six (four of these are spectrally discernible) due to the existence of *syn*- and *anti*-isomers as the *meso*-form (*R*,*S*-D) and the racemate (*S*,*S*-D and *R*,*R*-D).[78,79]

The *syn*:*anti* isomer ratio depends on the structure of the phosphapalladacycle [12,17,69] and on the nature of the solvent, but usually the *anti*-isomer is thermodynamically more favourable.[80] The fact that the dimeric cyclopalladated derivatives of trimesitylphosphine (HL^1) exist only as the *anti*-isomers [55] is attributable to the tendency for avoiding unfavourable through-space interactions between two bulky $PMes_2$ groups in the *syn*-isomer.

The drawbacks of the dimeric CPCs include also their dynamic behaviour, which often hampers recording the ^1H NMR spectra at room temperature. The μ-acetate PC-dimers having a half-open book conformation are the most fluxional.[2,22,51,59,68] The spectroscopic studies of the CN analogues have shown that the dynamic behaviour of these structures stems from the inversion of acetate bridges.[81,82] In the μ-halide PC-dimers, the central four-membered ring $\{Pd_2Hal_2\}$ is usually planar (according to X-ray diffraction);[83–85] some folding of the ring is observed only in sterically hindered complexes.[79,86] Nevertheless, in these dimers, too, exchange processes may take place due to the lability of the halide bridges. The fluxional behaviour of the μ-chloride CN-analogues was confirmed unambiguously using stereochemical criteria.[87]

The complications arising in the measurement of the NMR spectra of dimeric complexes caused by isomerism can be illustrated in relation to complex **6**. The pronounced signal broadening in its ^1H and ^{31}P NMR spectra recorded at 25 °C has been suggested [69] to be due to the interconversions of *syn*/*anti*-isomers and the atropoisomers of the eight-membered ring *A*.



6

This is confirmed by splitting of the ^{31}P NMR signals into eight peaks on lowering the temperature to −90 °C due to freezing out of the exchange processes. Previously, it has been suggested [58] that *syn* to *anti* transitions of the dimeric complexes are intramolecular. The presence of a signal close in position to that of the free HL^6 ligand in the low-temperature spectrum of dimer **6** may imply decoordination of the P-donor atom of one palladacycle, which opens up the way for the subsequent rotation around the Pd–C bond.[69]

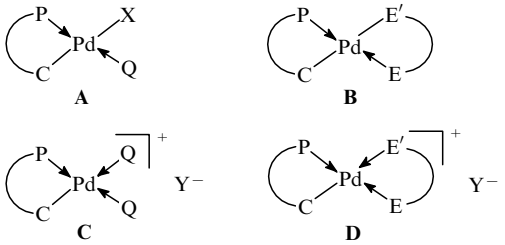
In the case of dimeric complexes **4b**–**d** with pyrazolate bridges, *anti*-isomers also tend to predominate in solutions.[64] However, the isomeric composition of these complexes depends on the degree of substitution of the bridging azolate heterocycle. Dimer **4d** with disubstituted 3,5-dmpz ligands exists as the *anti*-isomer both at room temperature and in the cold (−60 °C), whereas its analogues with unsubstituted (pz) and monosubstituted (4-mpz) pyrazolate bridges (**4b** and **4c**) exist as mixtures of *syn*- and *anti*-isomers in solutions at low temperature (^{31}P NMR data). The redistribution of isomers in favour of the latter (which is the only form at 20 °C) attests to the dynamic behaviour of the dimers. Presumably, the interconversion of geometric isomers in these structures takes place through the formation of mononuclear species with monodentate N-bonded pyrazolate.[64]

The combination of the properties of dimeric PC-complexes including poor solubility, isomerism and dynamic mobility makes them inconvenient for practical use and structural studies. The corresponding mononuclear derivatives are free from these drawbacks.

b. Mononuclear derivatives of PC-palladacycles

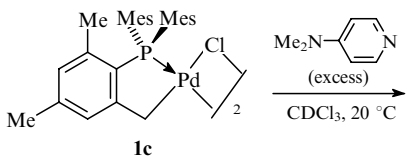
The mononuclear CPCs are used first of all for obtaining spectroscopic evidence for the structures of phosphapalladacycles. In addition, they are used in catalysis; some of them proved to be more efficient catalysts than the corresponding dimers.[14–18]

The structures of mononuclear PC-palladacycles are diverse: they depend on the nature of the auxiliary ligands incorporated in the molecule (the denticity, the charge and the nature of the heterodonor atoms) and on the steric crowding of this ligand and the PC-palladacycle. Depending on the charge of the auxiliary ligand, either neutral (**A**, **B**) or cationic (**C**, **D**) complexes containing monodentate (**A**, **C**) or bidentate (**B**, **D**) auxiliary ligands are formed.

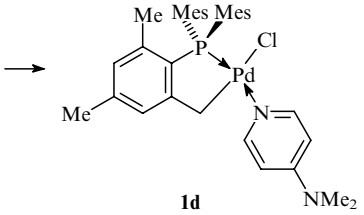


The mononuclear complexes of type **A** are the simplest derivatives of phosphapalladacycles; under certain conditions, they can even be the primary cyclopalladation products.[12] In the general case, these complexes are produced by cleavage of halide bridges in the dimers by monodentate auxiliary ligands. The possibility of such dimer monomerisation is largely determined by the steric requirements of the PC-palladacycle and the incoming ligand, the basicity of this ligand and the preferred geometric configuration of the resulting mononuclear adduct. Type **A** complexes are synthesised most often using phosphines and pyridine or its derivatives as auxiliary ligands. The reactions of PC-dimers with pyridine are usually carried out at room temperature.[54,60,88,89] The complete *in situ* conversion of the dimer into the monomer on treatment with a moderate excess of pyridine-d_5 in $CDCl_3$ opens up an easy way for obtaining spectroscopic (^1H NMR) characteristics of phosphapalladacycles.[90]

The influence of the basicity of the auxiliary ligand on the monomerisation of the PC-dimers has been elicidated in a spectroscopic study of the reaction of μ-chloride dimer **1c** [55,91] with pyridine derivatives. It was shown that this dimer readily reacts with highly basic 4-dimethylaminopyridine ($pK_a = 9.61$) to give mononuclear adduct **1d** but does not react (even on heating)



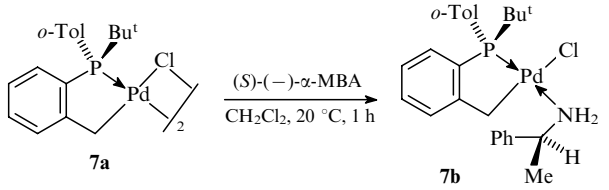
1c



1d

with analogous compounds containing electron-withdrawing 3-CN or 4-CO_2Me groups (pK_a = 1.35 and 3.51, respectively).[92]

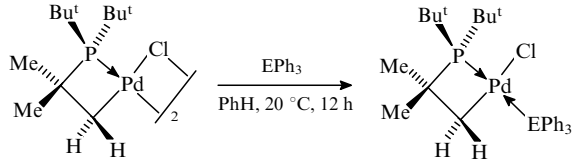
For the same reason, only the primary highly basic α-methylbenzylamine (α-MBA) was able to cleave the chloride bridges of dimer **7a** under mild conditions to give mononuclear derivative **7b**.[60]



7a **7b**

No adducts of PC-palladacycles with less basic monodentate tertiary amines are known. Attempts to introduce an amine of this type into the coordination sphere of a CN-palladacycle have failed.[93]

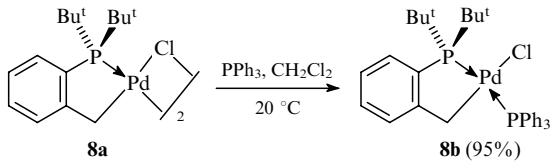
The nature of the donor atom of the auxiliary ligand is an important factor governing its affinity to palladium. This determines not only the ease but the mere possibility of its coordination to the PC-palladacycle. Thus a study of monomerisation of dimer **3b** under the action of related ligands like EPh_3 (E = P, As, Sb) has shown that only with triphenylphosphine does the reaction proceed readily under mild conditions to give mononuclear complex **3c**, whereas with $AsPh_3$ the reaction does not go to completion (complex **3d** largely dissociates in solutions due to the weaker Pd ← As bond), and in the case of $SbPh_3$, no reaction takes place for **3b**.[88,94]



3b **3c,d**

E = P (**3c**), As (**3d**).

The transformation of dimeric CPCs into monomers for structural studies is often accomplished using phosphines, the most popular of which is triphenylphosphine, a ligand with moderate steric requirements (the Tolman cone angle $\theta = 145°$).† The reactions of the PC-dimers (for example, dimer **8a**) with PPh_3 are usually carried out at room temperature in benzene [78,79,88,90] or dichloromethane,[58,69,96] or more rarely, acetone.[56] In some cases, due to the low solubility of the starting dimers or steric hindrance,[94] heating is required.[60,94,97–99]



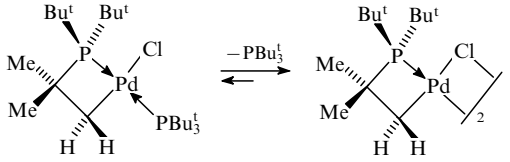
8a **8b** (95%)

A similar procedure is used to prepare adducts with other phosphines with relatively small molecules, for instance, PPh_2Me [88] and PMe_2Ph,[96] (θ = 127 and 136°, respectively), with phosphites $P(OMe)_3$,[58,69,74] $P(OEt)_3$,[69] and $P(OPh)_3$,[58,69,74,94] (θ = 107, 109 and 128°, respectively) [95,100] and with 5-phenyldibenzophosphole (DBP) [94] (see Supplement 1).

In the reactions of dimeric CPCs with P-donor substrates, the steric factors become crucial, while the basicity of the auxiliary ligand is less significant. As a consequence, even in the reaction with phosphines containing a donor phosphorus atom optimal for the coordination to palladium, the formation of mononuclear adducts can be prevented by steric restrictions. For example, a spectroscopic study (^{1}H and ^{31}P NMR) of the complexation of dimer **3b** with monodentate phosphines has shown that the strength of their binding with the PC-palladacycle decreases in the sequence given below:[88]

ER_3	PEt_3	~	PPh_2Me	~	PPh_3	>	PPr^i_3	>	PCy_3	~	PBu^t_2Me	>	PBu^t_3
θ	132		127		145		160		170		161		182
pK_a	8.69		4.57		2.73		–		9.70		–		11.40

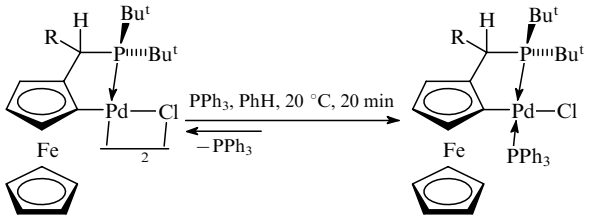
A comparison of the Tolman cone angles θ and the pK_a constants [101] demonstrates that this sequence is correlated with the increase in the ligand bulk but by no means with the basicity. The adducts with PEt_3, PPh_2Me, PPh_3 and PPr^i_3 (θ = 127–160°) are stable in the solid state and in solutions; complexes with more bulky phosphines, PCy_3 and PBu^t_2Me (θ = 170 and 161°, respectively), were prepared but they partly dissociate in solutions to give the starting dimer. In the case of sterically overcrowded adduct **3e** with the PBu^t_3 phosphine ligand (θ = 182°), the monomer ⇆ dimer equilibrium is shifted to the right almost completely, as indicated by the lack of spin–spin coupling between the two ^{31}P nuclei.[88,102]



3e **3b**

Moreover, an attempted recrystallisation of the isolated complex **3e** gave the starting dimer **3b**.[88,102,103] When bulky phosphines such as PBu^t_2Tol-*o* (θ = 186°) and PBu^t(Tol-*o*)$_2$ (θ = 190°) are made to react with PC-palladacycles, for example, with dimer **5a**, mononuclear derivatives are not formed for steric reasons.[57]

It is reasonable to assume that the steric crowding of the PC-palladacycle should also influence the efficiency of the reaction with phosphines. For example, the transformation of dimeric CPCs **9a** and **10a** with an unwieldy ferrocenyl core into the mononuclear derivatives **9b**, **10b**, containing even a small auxiliary ligand, PPh_3 (θ = 145°), does not proceed to completion when a strictly stoichiometric amount of the phosphine is used.[78,79] According to the ^{1}H and ^{31}P NMR spectra, the reaction mixture contains mononuclear adducts **9b**, **10b** together with the starting dimers **9a**, **10a** and the unreacted phosphine PPh_3.



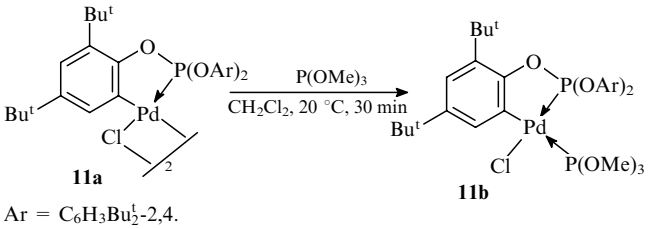
9a, **10a** **9b** (91%), **10b** (70%)

R = H (**9a**,**b**), Me (**10a**,**b**).

The equilibrium between the dimeric and monomeric complexes can be shifted towards the latter by using a slight (10%–15%) excess of the auxiliary ligand.[78,79] This method is also used in synthetic work [60,97,98] (see Supplement 1).

The steric obstacles are especially obvious in the monomerisation of cyclopalladated bulky phosphites. An attempt to monomerise the sterically overcrowded dimer **11a** by treating it with bulky tris(*o*-tolyl)phosphine (θ = 194°) has not met with success, whereas the small-size phosphite $P(OMe)_3$ (θ = 107°) readily reacts with dimer **11a** at room temperature to give adduct **11b**.[69]

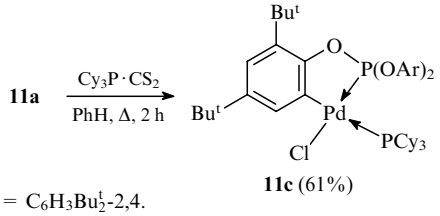
† Here and below, the Tolman cone angles θ were taken from Ref. 95



Ar = $C_6H_3Bu^t_2$-2,4.

Extra complications arise in the monomerisation of dimeric CPCs based on phosphites due to the forced (electronic requirements, see Section II.2.b) *cis*(P,P)-configuration of the resulting adduct. In this case, a bulky auxiliary ligand should be inserted into the Pd coordination sphere near the bulky $P(OC_6H_3Bu^t_2\text{-}2,4)_2$ fragment of the phosphite palladacycle. Note for comparison that dimeric CPCs based on phosphines (for example, dimer **3b**) react with bulky phosphines such as PBu^t_2Me, PCy_3 and P(Tol-*o*)$_3$ under mild conditions (20 °C) to give the *trans*(P,P)-complex.[88] In this case, the auxiliary ligand is inserted into the Pd coordination sphere near the methylene group (the least steric requirements) of the phosphine palladacycle.

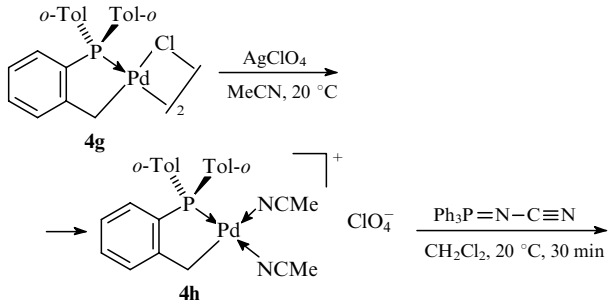
It is pertinent to mention a modified method for the synthesis of mononuclear phosphine derivatives of PC-palladacycles consisting of the use of the phosphine adduct with carbon disulfide instead of the free phosphine. Since the electron-enriched aliphatic phosphines (unlike aromatic phosphines) form rather stable adducts of the $Alk_3P\cdot CS_2$ type,[104] these adducts are destroyed only on heating. Only using this technique, was dimer **11a** completely converted into mononuclear adduct **11c** (this reaction with free phosphine does not proceed to completion).[69]

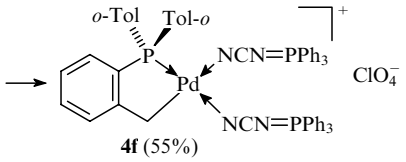


Ar = $C_6H_3Bu^t_2$-2,4.

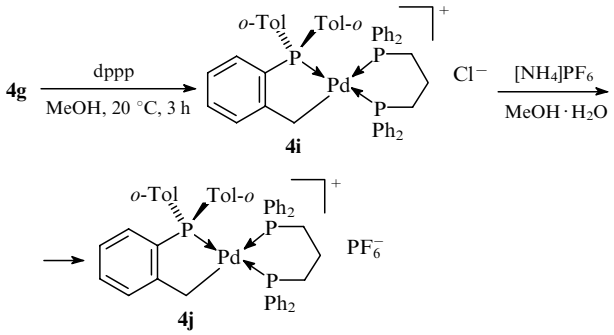
Although the true role of carbon disulfide in this reaction is not discussed in the study cited,[69] one cannot rule out the intermediate formation of species with the ylide phosphonium-dithiocarboxylate ligand $R_3P^+-CSS^-$ (see Ref. 104).

The cationic complexes of type **C** belong to the least studied class of phosphapalladacycle derivatives. The introduction of two monodentate neutral ligands into the reaction with the PC-palladacycle requires the preliminary removal of chloride ions from the dimeric precursor on treatment with silver salts. The reaction is carried out in a solvent capable of coordination, for example, in acetonitrile. A cationic bis(acetonitrile) adduct is formed intermediately and can be used for the subsequent introduction of other auxiliary ligands, including those with low coordinating capacity. The synthesis of bis(iminophosphorane) derivative **4f** from cyclopalladated tris(*o*-tolyl)phosphine **4g** through acetonitrile intermediate **4h** can serve as an example of using this approach.[105]





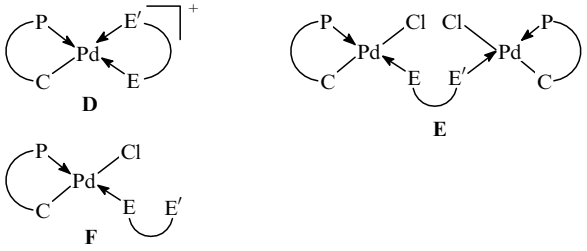
Cationic complexes of type **D** are formed upon coordination of non-charged bidentate ligands to a phosphapalladacycle. Under the optimal conditions, these derivatives can be obtained directly from μ-chloride dimeric CPCs. In most cases, the reaction is carried out at room temperature. The direct reaction of the μ-chloride dimer with a neutral chelating reagent gives rise to ionic complex **D** with the outer-sphere chloride.[58, 60, 69] The introduction of the $[NH_4]PF_6$, KPF_6 or $NaClO_4$ salts either directly or in the second stage of the reaction (after chelation of the auxiliary ligand) allows these adducts to be isolated as hexafluoro-phosphates[90] or perchlorates[56] (see Supplement 1). This technique was used to prepare ionic complexes **4i** or then **4j** from dimer **4g**.[30]



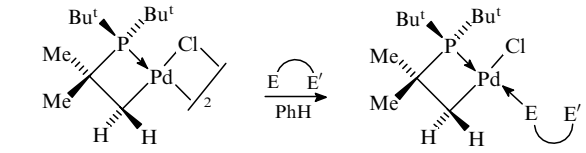
dppp is $Ph_2P(CH_2)_3PPh_2$.

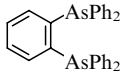
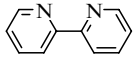
The obvious gain in entropy caused by binding of bidentate ligands compared to monodentate ligands is partially counterbalanced by the necessity of replacement of two halide ligands in the initial dimer (instead of mere cleavage of halide bridges). As a consequence, the rules for complexation of phosphapalladacycles with mono- and bidentate ligands become similar in many respects.

Detailed studies of the complexation of μ-chloride dimer **3b** with a number of potentially bidentate ligands[106] have shown that the ligand structure has a pronounced effect on the course of the reaction. Under unfavourable conditions, type **E** and **F** complexes with bridging or monodentate ligands, respectively, are formed instead of the expected κ^2-chelation (complex **D**).

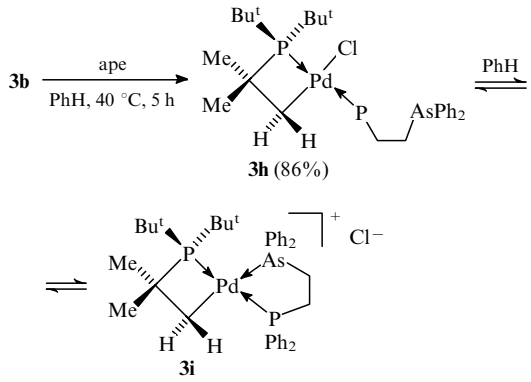


As was to be expected, the chelating properties of the ligand depend, first of all, on the nature of the donor atoms (P > As > N); this is most important for their reactions with μ-halide dimers. As opposed to the easy chelation attained with diphosphines, dppe [bis(diphenylphosphino)ethane][58, 69] and dppp,[30] the As,As- (diars) and N,N-donor (bipy) ligands behave as monodentate in the reaction with dimer **3b**. Even with a twofold excess of the ligand (for diars) or on raising the temperature (for bipy), only neutral adducts **3f**, **3g** are formed.[106]



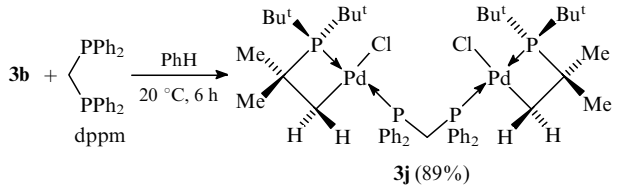
E E′ =  (diars, **3f**),  (bipy, **3g**).

A similar reaction of complex **3b** with a P,As-donor ligand (ape) also gave mononuclear derivative **3h** of type **F**; however, according to ^{31}P NMR spectroscopy, it is equilibrated in solutions with cationic complex **3i** of type **D**:



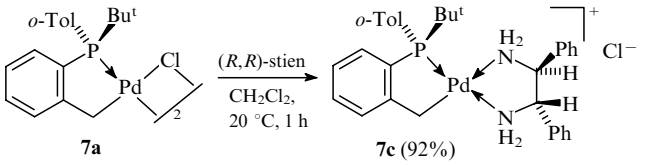
ape is $Ph_2P(CH_2)_2AsPh_2$.

The coordination mode of the potentially bidentate ligands also depends on the length of the fragment that separates the donor atoms and determines the size of the chelate ring. Methylenediphosphines are known [107–109] to possess low susceptibility for chelation (in particular, in the reactions with palladacycles [110–113]) due to the strain in the four-membered $\{MP_2C\}$ ring thus formed. Therefore, it is not surprising that bis(diphenylphosphino)methane (dppm) reacts with μ-chloride dimer **3b** as a bridging ligand to give non-charged dimer **3j** of type **E**, despite the presence of two optimal donor atoms of phosphorus:[106]



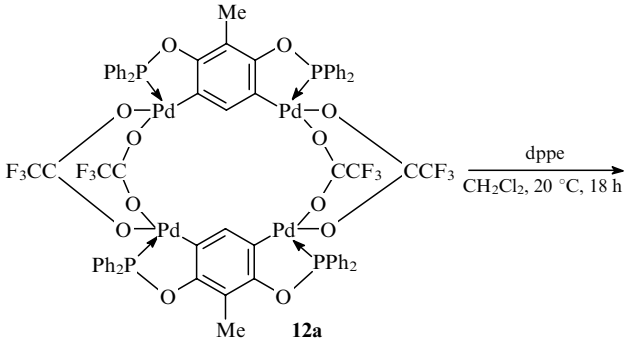
Probably, the chelation of dppm with PC-palladacycles could be accomplished by dehalogenating the starting μ-Cl-dimers, because the efficiency of this approach for CN-analogues is well known.[110, 111, 113, 114]

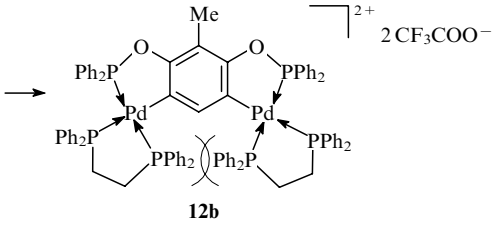
The chelation properties of N,N-donor ligands are enhanced with an increase in their basicity and a decrease in the steric requirements. Thus (*R*,*R*)-1,2-diamino-1,2-diphenylethane (stien), containing two primary amino groups, directly reacts with μ-chloride dimer **7a** under mild conditions to give cationic complex **7c** in a high yield, despite the steric crowding of the phosphine ligand.[60]



This reaction can be carried out *in situ*, which is especially important for solving some stereochemical problems.[90]

The success of chelation using potentially bidentate ligands with dimeric PC-palladacycles is also determined by the ability of bridging anions to compete for the metal. The situation is simplified upon the replacement of bridging halide ligands by harder anions. For example, binuclear derivative **12b** is formed as the major product when tetranuclear complex **12a**, containing trifluoroacetate bridges, reacts with diphosphine dppe.[115]

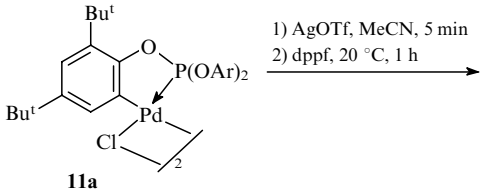


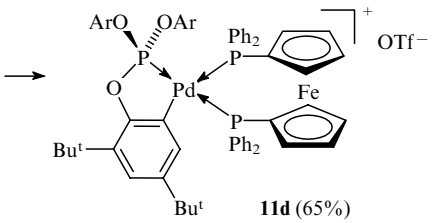


The researchers noted the formation of a minor amount of a compound with bridging diphosphine ligands, probably having a tetranuclear structure similar to the structure established by X-ray diffraction for the starting complex **12a**.‡

This side process might be due to steric restrictions between the neighbouring PPh_2 groups of two diphosphines dppe chelated to the metal atoms of the doubly cyclopalladated bis(phosphinite) H_2L[12].

An efficient solution to the problem of anion competition in the formation of type **D** complexes is the removal of chloride ions from the metal coordination sphere in the starting dimer on treatment with an appropriate silver salt, for example, triflate [69] or hexafluorophosphate.[106] The reaction with AgOTf is usually carried out in acetonitrile in two steps with intermediate generation of the reactive bis(acetonitrile) adduct of the PC-palladacycle, which is then made to react with an auxiliary ligand. Using this method, successful chelation of 1,1′-bis(diphenylphosphino)-ferrocene (dppf) with the phosphite palladacycle of dimer **11a** was accomplished.[69]



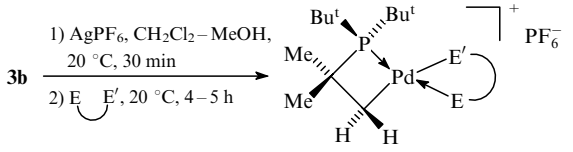


Ar = $C_6H_3Bu^t_2$-2,4.

‡ The synthesis of the complex **12a** is the first example of double cyclopalladation of P-donor substrates at the same benzene ring.

It should be noted that an attempt to prepare complex **11d** by direct reaction of μ-chloride dimer **11a** with diphosphine dppf (CH_2Cl_2, 20 °C, 30 min) has not met with success, a complex mixture of products being formed under these conditions.[69]

The dehalogenation of μ-chloride dimers under the action of $AgPF_6$ is carried out in a mixture of dichloromethane with methanol; AgCl is removed before the addition of the auxiliary ligand to the solution of the intermediate solvated PC-palladacycle. The cationic complexes **3k**, **3l** and **3m** with the ape, diars and bipy ligands having low coordinating abilities have been obtained by this method in quite acceptable yields.[106]

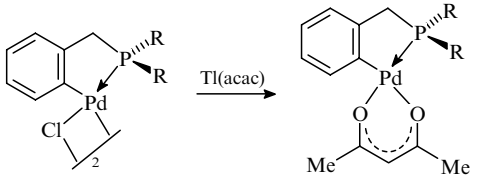


3k (78%), **3l** (74%), **3m** (69%)

E E′ = ape (**3k**), diars (**3l**), bipy (**3m**).

The neutral complexes of type **B** are formed upon chelation of PC-palladacycles by anionic ligands. Although the ionic type of these ligands (which are used as Na, K or Tl salts) essentially eliminates the possibility of competition of the bridging halides of the starting CPC dimer for the metal, some synthetic problems still remain. As auxiliary ligands in the synthesis of type **B** complexes, β-diketonates,[54, 57, 60, 97] dithiocarboxylates,[53, 69] pyrazolylborates,[116] prolinates [79, 117] and 2-acylphenolates [118] have been used (see Supplement 1).

For the spectral investigations of PC-palladacycles, complexes with the symmetric acetylacetonate (acac) ligand are most convenient. The acetylacetonate complexes possess a number of advantages: first, the ^{1}H NMR spectrum of the acetylacetonate ligand is 'transparent' (the ligand gives rise to only three additional singlets); second, the volatility of the neutral complexes allows the use of mass spectrometry in the studies of PC-palladacycles.[54, 119] For the synthesis of acetylacetonate complexes from μ-chloride dimers, fairly toxic thallium salt Tl(acac) is normally used; with rare exceptions,[57] the yields are relatively low (40% – 70%)

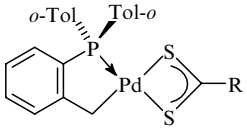


2a, **5a** **2f** (41%), **5e** (94%)

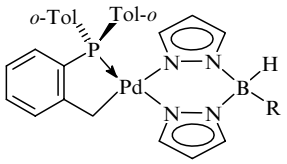
R = Ph (**2a**,**f**), Bu^t (**5a**,**e**).

The replacement of Tl(acac) by K(acac) was of low utility. Acetylacetonate derivative **10c** has been prepared from dimer **10a** in only a 28% yield,[90] although the yields of the corresponding complexes in the reactions of K(acac) with CN-palladacycles reach 97%.[120] It is worth noting that transition from dimeric PC-complexes to the mononuclear type **B** β-diketonate derivatives and the subsequent modification of auxiliary ligands (for example, the replacement of the methyl groups in the acetylacetonate ligand by trifluoromethyl groups) may markedly enhance the catalytic activity of phosphapalladacycles.[22]

The dithiocarboxylate and bis(pyrazolyl)borate ligands are also symmetric. The dithiocarbamate (**4k**) and xanthate (**4l**) derivatives of the PC-palladacycles have found application in the synthesis of bi- and polynuclear heterometallic compounds.



R = NMe_2 (**4k**), OEt (**4l**)

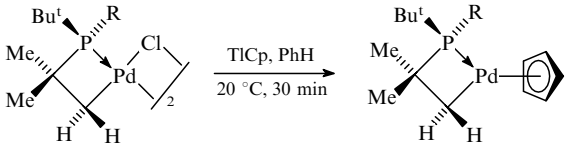


R = H (**4m**), pz (**4n**)

Thus the reactions of dithiocarboxylate complexes with Lewis acids such as HgX_2,[53, 121, 122] $AgClO_4$ and $[M(OClO_3)(PPh_3)]$ (M = Ag, Au),[123] have resulted in bimetallic Pd,M complexes in which the metal atoms are connected by bridging sulfur atoms.

The modification of dimer **4a** with poly(pyrazol-1-yl)boronates to give complexes **4m**,**n** has been designed to facilitate the oxidative addition of electrophiles (MeI, ArBr, *etc*.) to the metal and to stabilise the Pd(IV) centre in the resulting cyclopalladated complex through increasing the nucleophilicity of the Pd(II) centre.[116] Unfortunately, these attempts have failed.

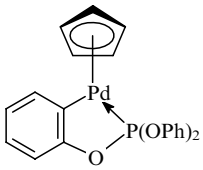
Cyclopentadienyl derivatives of phosphapalladacycles occupy a special position among mononuclear complexes of type **B**, because the auxiliary ligand is η^5-coordinated instead of being κ^2-bound through two heteroatoms. These complexes are synthesised by treatment of the corresponding μ-chloride dimers (for example, **3b** or **13a**) with TlCp or LiCp* (Cp* is pentamethylcyclopentadienyl) in benzene [124] or THF [58, 59] at room temperature. Complexes with the Cp^- ligand have been obtained in quite satisfactory yields (67% for R = Ph and 77% for R = Bu^t), whereas the yields of complexes with the bulky Cp^{*-} ligand are much lower (39% for R = Ph and 60% for R = Bu^t).[124]



3b, **13a** **3n**, **13b**

R = Bu^t (**3b**,**n**), Ph (**13a**,**b**).

The number of complexes in which the PC-palladacycle is bound to the η^5-Cp [58, 59, 124] or η^5-Cp* ligand [124] is limited to derivatives of two cyclopalladated phosphines (PBu^t_3 and $PPhBu^t_2$) [124] and two phosphites, $[P(OPh)_3$ [58] and $P(OTol\text{-}o)_3$ [59]] (see Supplement 1). The η^5-coordination of the auxiliary ligand in complex **14a** was confirmed by X-ray diffraction; however, the ligand is bound to the metal non-symmetrically, the Pd – C(Cp) bond lengths varying in the range of 2.284(7) – 2.347(9) Å.[58]



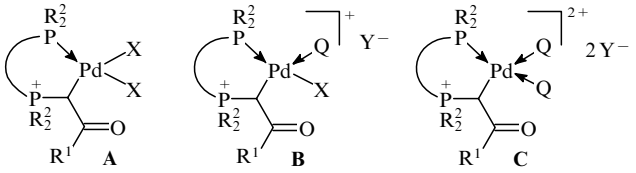
14a

To conclude this Section, let us consider the possibility of back monomer → dimer transformation. The success of this transformation is determined, first of all, by the nature of the donor atoms of the auxiliary ligand and its denticity. The removal of the mono- or bidentate ligands with relatively rigid N- and O-donor atoms from the coordination sphere of the palladacycle is attained by mere protonation of the auxiliary ligand (for example, with dilute HCl).[79, 90, 117, 125] The situation becomes much more complicated on passing to adducts with phosphine ligands due to stronger binding of the soft P-donor atom with the soft Pd(II) centre. Nevertheless, the monodentate phosphines can be

removed using a method elaborated for CN systems,[126] namely, by treatment of the adduct with an excess of a cheap bidentate ligand, ethylenediamine (en), in a biphasic system (for example, in the dichloromethane – water system).[90, 127, 128]

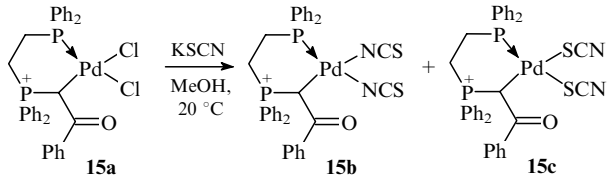
c. Phosphino-P-ylide complexes

Due to the formal neutrality of zwitter-ionic phosphino-P-ylide ligands, the forms of existence of the metallacycles they form (**A** – **C**) differ from those for classical PC-systems. Chelation with these ligands yields mononuclear compounds of type **A** with five-[129–133] or six-membered [129–137] PC-palladacycles or bis(chelate) *spiro*-complexes.[138] Binuclear compounds with phosphino-P-ylide ligands have not been reported as yet. The ways for modification of the metal coordination environment in these systems are reduced to variation of the nature of the anions in type **A** complexes and the introduction of one or two neutral monodentate ligands, resulting in mono- (**B**) or dication (**C**) derivatives, respectively. In both cases, halide replacement takes place.

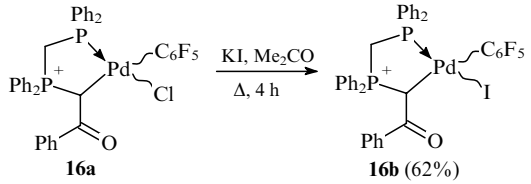


This constitutes the key difference between the reactions of phosphino-P-ylide PC-complexes and those typical of classical dimeric PC-systems in which labile halide bridges are cleaved.

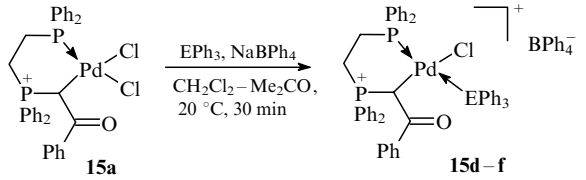
Perhaps, for this reason, the replacement of two chloride ions in type **A** complexes by softer halides (Br^-, I^-) or by a pseudohalide (SCN^-) on treatment with simple salts, NaBr, NaI or KSCN, under mild conditions ($MeOH-CH_2Cl_2$, 20 °C) gives the target products in moderate yields (24% – 59%).[130, 131] This can be illustrated by the transformation of dichloride **15a** into isothiocyanate derivative **15b** in 26% yield. It is worth noting that two isomers, **15b** and **15c** (1 : 2) containing N- and S-bound anions, respectively, exist in solutions (IR data).[130]



The metathesis of anions in monoarylated complexes [ArPd(η^2-L)Cl] requires long-term heating of the chloride precursor with KBr, KI or KSCN in acetone, but the yields of modified complexes (for example, **16b**) increase in this case to 62% – 73%.[133]

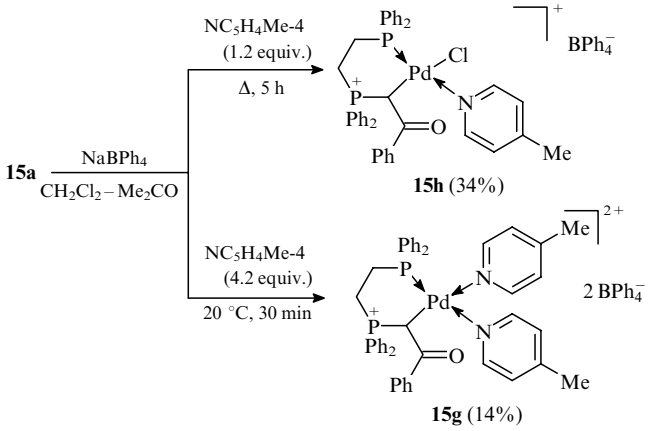


A monodentate neutral auxiliary ligand can be attached to a phosphino-P-ylide palladacycle only after dehalogenation of the dichloride precursor, for example, on treatment with sodium tetraphenylborate.[131, 132, 136] Reactions of this type are usually carried out under mild conditions, irrespective of the coordinating ability of the incoming ligand, which can be represented by phosphines, phosphites, arsines, or stibines or N-donor ligands (see Supplement 2).



E = P (**15d**, 39%), As (**15e**, 41%), Sb (**15f**, 37%).

Using this method, it is even possible to introduce two auxiliary neutral ligands into the coordination to a phosphino-P-ylide palladacycle, which is indicative of the efficiency of this approach. The substitution of N-donor ligands for the two halides in the dichloride precursor **15a** (bis-adducts **15g**) can be attained by using a four-fold excess of 4-methylpyridine; the reaction with an equimolar amount of the auxiliary ligand yields monoadduct **15h**.[132]



Although dicationic complex **15g** has been isolated in a low yield, this reaction is of interest, because structures of this type are rather seldom encountered among both classical PC-palladacycle derivatives [105] and their CN-analogues.[5, 47, 111]

The cationic phosphino-P-ylide complexes, formed in the reactions with neutral monodentate ligands (see Supplement 2), are less stable [132, 136] than neutral dichloride precursors such as [Pd(η^2-L)Cl_2], which are resistant against oxidants and heating.

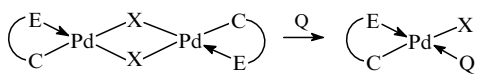
Apparently, attempts at direct substitution of monodentate ligands for the chloride in type **A** precursor are impracticable due to the lower stability of phosphino-P-ylide palladacycles compared to the classical PC-analogues. For example, partial decomposition of dichloride complexes of type **A** with evolution of free ligands L^n has been detected by IR spectroscopy on refluxing in pyridine.[130] Analysis of the dependence of the degree of destruction on the structure of the complexes showed that the stability of phosphapalladacycles of this type depends on their size (five-membered rings are more stable than six-membered rings) and on the electronic effects of substituents at the carbonyl group (Ph > Me > MeO).[130]

2. Regioselectivity of ligand coordination to phosphapalladacycles

The problem of determining the geometric configuration of complexes formed upon the coordination of additional ligands to palladacycles arises necessarily in relation to structural studies or practical use. For example, when palladacycles are used as catalysts, it is pertinent to have an idea of the regiochemistry of particular stages of the catalytic cycle. The regiochemistry of the coordination of additional ligands to palladacycles is one more feature which distinguishes PC-palladacycles from their CN-analogues.

a. General views on the regiochemistry of coordination to palladacycles

Palladium complexes are usually classified as labile. It is known that their reactions in solutions are many orders of magnitude faster than the reactions of platinum analogues.[139] Therefore, it is natural to assume that the regiochemistry of the reactions of palladacycles with auxiliary ligands is determined by thermodynamics rather than the kinetics of these processes. This accounts for the fact, surprising at first glance, that the monodentate auxiliary ligand is inserted predominantly (in some cases, exclusively) into the *trans*-position to the heterodonor atom of the palladacycle in the dimeric CPC rather than to the carbon atom, which has a higher capacity for labilisation of the *trans*-located Pd – Hal bond.



A **B**

A distinctive feature of CN-systems is the high regioselectivity of monomerisation of the dimeric complexes by auxiliary ligands. In the vast majority of cases, the monodentate N- and P-donor ligands are inserted into the coordination sphere of the CN-palladacycle in the *trans*-position to nitrogen.[140–144] Exceptions to this rule are few[145–147] and refer only to pyridine adducts, whereas the formation of monophosphine derivatives with the *trans*(P,C)-geometry is either impossible,[111] or these complexes are highly unstable and highly reactive.[148] The introduction of phosphine into the *trans*-position to the carbon atom becomes possible only after removal of the halide and blocking of the *cis*-position. For example, bis(phosphine) derivatives $[Pd(C^{\frown}N)(PAr_3)_2]^+$ have been prepared in this way.[149]

This high selectivity is usually attributable to the anti-symbiosis phenomenon according to which the *trans*-coordination of two soft ligands to a transition metal destabilises the system.[150,151] Recently, more expressive terms, 'transphobia'[111,113,152,153] and '*trans* choice',[154] have been proposed for interpreting the regioselectivity of reactions of CPC with Lewis bases within the framework of the same antisymbiosis concept. All three concepts can be substantiated in terms of the Maximum Hardness Principle (MHP) proposed by Pearson.[155,156] According to this principle, structures (or systems) with the maximum energy difference between the occupied and vacant orbitals possess the highest thermodynamic stability. A softer molecule has a more diffuse electron shell and is more reactive.

The '*trans* choice' principle is underlain by the concept of stabilisation of square planar complexes with *trans*-arrangement of the 'softest' and the 'hardest' ligands in the coordination sphere.[154] To predict the regiochemistry of the reactions of palladacycles using this concept, one needs quantitative characteristics of the 'softness' or 'hardness' of the donor atoms in the palladacycle and the additional ligands present in the coordination sphere. Since such information is unavailable without calculations, the use of this concept is limited to qualitative analysis.

The 'transphobia' concept[113,152] appears more attractive, as it opens the way for some quantitative considerations. In this case, analysis of the differences in the stability of different geometric configurations is based on comparison of the *trans*-effects of two pairs of ligands on the diagonals of the square planar complex. The essence of this concept is the assumption that the degree of destabilisation of complexes increases with an increase in the *trans*-effect of both partners. If only donor atoms (X, Y, C) of the ligands bound to the metal are taken into account, then, in the most general form, the transphobia (which has been proposed to be designated by the letter T[152]) sequence for pairs of donors located on one diagonal is as follows:[111,113,152]

X/Y (X, Y = Hal, N, P) ≈ C/X (X = Hal, N) < C/P < C/C.

Among the rules found for the coordination properties of CN-palladacycles, the following deserves attention: (1) greater *trans*-effect of σ-bonded aryl groups compared to phosphines entails an increase in the transphobia in ligand pairs in the sequence $PR_3/PR_3 < Ar/PR_3 < Ar/Ar$;[111] (2) the antisymbiotic effect for triarylphosphines is higher§ than for trialkylphosphines ($PAlk_3 < PAr_3$);[111,113] (3) the transphobia for any ligand pair increases on passing from platinum to palladium.[111,113,152] The transphobia concept predicts high reactivity for the complexes in which ligands with high *trans*-effects are located on the same diagonal.[113,148,149,152]

The applicability of the transphobia concept to CN-systems has been confirmed by vast experimental data.[111,113,148,149,152,153,161,162] However, in the general case, this concept does not fully explain the significant difference between the PC-palladacycles and CN-systems, namely, the lower (in some cases, inverted) regioselectivity of binding of monodentate and non-symmetrical bidentate ligands. Apart from the expected dependence on the behaviour of the incoming ligand, the regioselectivity of the phosphapalladacycle coordination with additional ligands depends, to a considerable extent, on the features of the PC-palladacycle. The nature of the P-donor atom (phosphine, phosphinite or phosphite) is most important, first of all, due to different relationships between the σ-donor and π-acceptor properties. The hybridisation of the C-donor atom (sp^2 or sp^3) and steric effects may also be significant. Depending on the combination of these factors, mononuclear derivatives of PC-palladacycles can form as *cis*- or *trans*-isomers or an isomer mixture.

b. The *trans*-effect in palladacycles

The ligand *trans*-effect discovered by Chernyaev in the beginning of the 20th century has been studied in detail both experimentally and theoretically.[158,163–166] The terminology used in this field has been markedly changed through the years. Originally, the terms '*trans*-influence' and '*trans*-effect' have been used in the literature to refer to the static (ground state) and dynamic (kinetic, transition state) aspects of the phenomenon. In our opinion, these terms do not reflect the key difference between these two variables. The terms 'structural *trans*-effect' (STE) and 'kinetic *trans*-effect' (KTE) used more recently are much more informative.[166]

Due to the known lability of palladium compounds,[139] consideration of the regiochemistry of reactions of palladacycles may be limited to the use of static (thermodynamic) parameters describing the structural *trans*-effect (STE). Unfortunately, despite the long-standing history of development of the views on the *trans*-effect, the main bulk of studies concerning the quantitative *trans*-effect refers to platinum compounds.[158,163–166] The information on palladium complexes,[160,167] the more so, organopalladium compounds,[168,169] in particular, cyclometallated ones,[161,170] is extremely scarce. Although it is believed[159] that derivatives of metals with similar electron configurations do not differ much in properties, the transfer of general rules from one metal to another may bring about distortions.

The few known data on the *trans*-effect of ligands in organopalladium compounds demonstrate that only general trends are retained on passing from platinum to palladium. For instance, on the basis of comparison of the chemical shifts of metallated sp^2-hybridised carbon atoms in the ^{13}C NMR spectra of a series of CPCs of the type $[PdX(C^{\frown}N)(PPh_3)]$, the following STE sequence for the X^- anions was established: $CN^- < SCN^- < Cl^- < Br^- < I^-$.[170] This sequence is consistent with the general views on the halide STE in platinum coordination compounds ($F^- < Cl^- < Br^- < I^-$ [139,159,165]). A similar (but not identical) order of variation of the halide STE has been found by analysis of

§ This conclusion contradicts the results of quantitative estimates of the *trans*-effect of various phosphines in platinum complexes obtained by X-ray diffraction[157] and IR[158,159] and NMR spectroscopy,[157,159,160] according to which it decreases in the sequence $PEt_3 \approx PBu_3 > PMe_2Ph > PPh_3$.

X-ray diffraction data for the *trans*-[PhPdX(PPh_3)$_2$] complexes (X = F, Cl, Br, I): $F^- < Cl^-$; $Br^- < I^-$; but $Cl^- \geqslant Br^-$.[169] However, the positions of the cyanide and the thiocyanate ions in the series of STE found for CPCs [170] differ from those typical of coordination compounds of platinum ($Cl^- < I^- \approx SCN^- < CN^-$ [139, 158, 159]). These deviations may be due to different contributions of the σ- and π-constituents of the M–L bond (L is the ligand) located in the *trans*-position. In the case of platinum, the order of anions changes on passing from σ-STE ($SCN^- < CN^- > Br^- \approx Cl^-$ [164]) to π-STE ($CN^- < SCN^-$ [164]). The STE for carboxylate anions in palladium compounds has not been estimated; however, it can be assumed (by analogy with platinum compounds [159, 160, 163]) that the effect of these O-donor anions should be least pronounced. For example, according to IR data (ν_{Pt-H}), the STE of anions increases in the sequence $NO_3^- < CF_3COO^- < ArCOO^- < NCO^- \approx NCS^- \approx Cl^- \approx Br^- < I^- \approx SCN^- < CN^-$.[158, 159]

X-Ray diffraction data for a large series of iminoacyl palladium complexes including CO-type CPCs were used to determine the relative STE values for C- and N-donor ligands and for iodide in these complexes: bipy < I^- < σ-C(sp^2)$^-$ (see Ref. 161). This sequence is consistent with the STE series for platinum complexes derived from IR spectroscopy data (ν_{Pt-H}): Py ≈ $MeNH_2$ < I^- < $PhC{\equiv}C^-$.[58, 159] However, the NMR spectra (J_{Pt-P}) give a somewhat different sequence: I^- < Py < Et_2NH < Me^- < Ph^-.[158–160]

The results of studies of the STE of heterodonor ligands in palladium compounds [168] imply that this effect is most pronounced in P-containing ligands. For example, it was found that in the palladium coordination complexes [Pd(X⌒Y)Cl_2] with the bidentate ligands X⌒Y, the STE decreases in the sequence $Ph_2P⌒PPh_2$ > $Ph_2P⌒SMe$ > $Ph_2As⌒SMe$.[167] For the allyl complexes [Pd(η^3-All*)(O⌒X)]BF_4 (All* = 2-methylallyl; O⌒X = XCH_2COOEt, where X = PPh_2, NPh_2, OPh, SPh, NC_5H_5), a similar dependence has been found: $PPh_2 \gg NPh_2 \approx$ OPh > SPh > NC_5H_5.[168] These sequences are mainly in line with the STE scale established for platinum coordination complexes using X-ray diffraction data (from comparison of the Pt–Cl bond lengths): $PPh_3 > AsPh_3 > Me_2S \approx Ph_2S > NH_3$.[157]

c. Estimation of the *trans*-effect of P- and C-donor atoms in phosphapalladacycles

It can be seen from the foregoing that the studies on the structural *trans*-effect of ligands in palladium(II) complexes and, the more so, in organometallic types of complexes are few. The total lack of any information on the STE in phosphapalladacyclic structures and the inconsistency of some conclusions, drawn using different criteria, concerning the ligand *trans*-effect in platinum(II) coordination compounds promote the search for more legitimate ways for estimating the STE in PC-palladacycles of various types. To interpret and/or predict the regiochemistry of the coordination of palladacycles with an additional ligand, it is necessary first to compare the STEs of a carbon and a heterodonor atom of the palladacycle.

Since a large number of publications deal with the X-ray diffraction analysis of the PC- (Table 1) and especially CN-palladacycles (Table 2), we used X-ray diffraction data to tackle this problem. The PC-palladacycles in which the metal is bound either to two identical anions [dimeric CPCs with chloride (**1c**, **3b**, **6**, **9a**, **11a**, **17**–**21**), bromide (**3o**, **22**), iodide (**4o**) and carboxylate (**4a**, **7d**, **12b**) bridges] or with bidentate symmetrical auxiliary ligands [mononuclear derivatives of PC-palladacycles (**11e**, **23a**), their phosphino-P-ylide analogues (**16c**) and the dichlorides of the latter (**15a**, **24**)] were used as models. Comparison of the lengths of bonds formed by the metal with two identical atoms that occupy *trans*-positions relative to the carbanionic and heterodonor centres, provides the most correct view on the relative STEs of the two 'ends' of the ligand enclosed in a palladacycle.

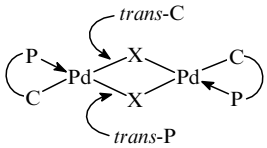


Table 1 presents the lengths of two Pd–X bonds (X = Cl, Br, I, O, S or P) that occupy the *trans*-positions with respect to C- and P-donor atoms of phosphapalladacycles and the difference

Table 1. *trans*-Effect of P- and C-donor atoms in PC-palladacycles.

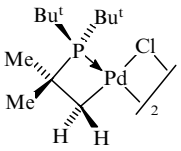
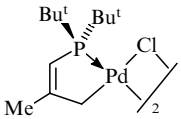
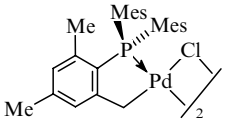
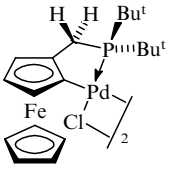
Structure	Number of the compound	C-Donor	P-Donor	l(Pd–X) /Å		Δl /Å	Code [a]	Ref.
				trans-P	*trans*-C			
				X = Cl				
	**3b**	CH_2	PBu^t_2	2.429	2.474	0.045	BIHLOT01	171, 172
	**17**	$AllCH_2$	PBu^t_2	2.416	2.455	0.039	CAFFOE	83
	**1c**	$ArCH_2$	$PMes_2$	2.400 2.415	2.487 2.472	0.087 0.057	VANHEX	85
	**9a**	Fc	PBu^t_2	2.426 2.404	2.446 2.445	0.020 0.041	QALNUM	79

Table 1 (continued).

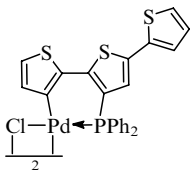
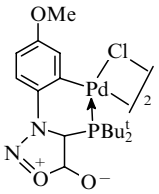
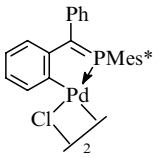
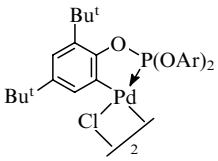
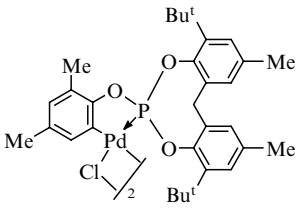
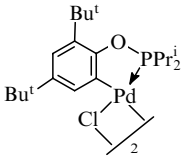
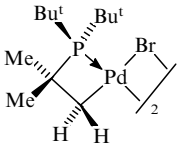
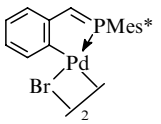
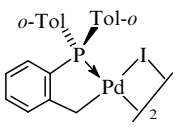
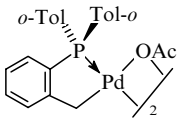
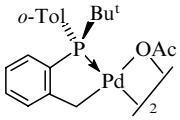
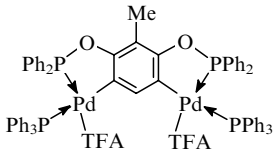
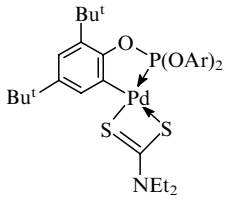
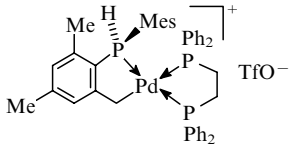
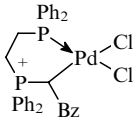
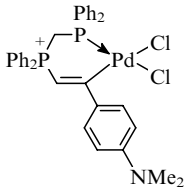
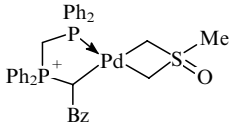
Structure	Number of the compound	C-Donor	P-Donor	l(Pd – X) /Å		Δl /Å	Code [a]	Ref.
				trans-P	*trans*-C			
				X = Cl				
	**18**	thienyl	PPh_2	2.425	2.418	−0.007	QANLAS	173
	**19**	Ar	PBu^t_2	2.436 2.425	2.442 2.435	0.006 0.010	NAJXEB	174
 (Mes* = 2,4,6-$Bu^t_3C_6H_2$)	**20**	C_6H_4	C = PMes*	2.389	2.438	0.049	TUHBON	86
 (Ar = 2,4-$Bu^t_2C_6H_3$)	**11a**	Ar	$OP(OAr)_2$	2.407	2.418	0.011	GEGRAL	175
	**6**	Ar	$OP(OAr)_2$	2.390 2.399	2.408 2.413	0.018 0.015	OJUBOK	69
	**21**	Ar	$OPPr^i_2$	2.4313	2.433	0.002	OMAWEE	17
				X = Br				
	**3o**	CH_2	PBu^t_2	2.550	2.592	0.042	FORXIT	176
	**22**	Ar	C = PMes*	2.508	2.560	0.052	REMQAB	177
				X = I				
	**4o**	$ArCH_2$	P(*o*-Tol)$_2$	2.665	2.723	0.058	CODJAG	84

Table 1 (continued).

Structure	Number of the compound	C-Donor	P-Donor	l(Pd – X) /Å		Δl /Å	Code [a]	Ref.
				trans-P	*trans*-C			
				X = OCOR				
	**4a**	$ArCH_2$	P(*o*-Tol)$_2$	2.111	2.147	0.036	ZEPHOR	1, 2
				2.127	2.134	0.007		
				2.118	2.149	0.031		
				2.111	2.156	0.045		
	**7d**	$ArCH_2$	PBu^t(*o*-Tol)	2.120	2.136	0.016	ABTPBP	178
				2.124	2.209	0.085		
				2.119	2.155	0.037		
 (TFA is trifluoroacetate)	**12b**	Ar	$OPPh_2$	2.141	2.149	0.008	OJOLAA	115
				2.145	2.151	0.006		
				2.143	2.150	0.007		
				X = S				
 (Ar = 2,4-Bu$^t_2$C$_6$H$_3$)	**11e**	Ar	$OP(OAr)_2$	2.3739	2.3719	0.002	OJUBIE	69
				X = P				
	**23a**	$ArCH_2$	C(sp^2)PHMes	2.381	2.415	0.034	–	179
				X = Cl				
	**15a**	BzCH	C(sp^3)PPh$_2$	2.390	2.340	−0.050	–	137
	**24**	C=C(Ar)	C(sp^3)PPh$_2$	2.378	2.394	0.016	WOKYIE	180
				2.384	2.367	−0.017		
				X = C				
	**16c**	BzCH	C(sp^3)PPh$_2$	2.103	2.087	−0.016	VETNUD	138

[a] Code in the Cambridge Structural Database.

between them (Δl), which characterises the difference between the STEs of these atoms.

In order to compare the regiochemistry of coordination of additional ligands to palladacycles containing P- and N-heterodonor atoms, the corresponding parameters for CN-systems are given in Table 2 (taking the five-membered CN-palladacycles containing amine, imine or heterocyclic nitrogen atom as examples).

The Δl parameters given in Tables 1 and 2 indicate that PC- and CN-palladacycles are essentially different. In the case of CN-dimers with various C- and N-donors (see Table 2), the Δl_{av} parameters averaged for each group vary in the ranges of 0.115 – 0.180 and 0.094 – 0.103 Å for μ-halide and μ-carboxylate dimers, respectively, thus demonstrating a substantial difference between the STE values of C- and N-donor atoms of the palladacycle. These values imply a high degree of selectivity in the

Table 2. *trans*-Effect of N- and C-donor atoms in five-membered CN-palladacycles (on the basis of structural parameters of dimeric CPCs).

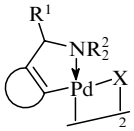
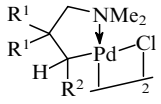
No.	Structure elements [a]		R^1	l(Pd – X) /Å		Δl /Å	Ref.
	C-Donor	N-Donor		*trans*-C	*trans*-N		
							
				X = Cl			
1	{(η^5-Cp)Fe(η^5-C_5H_2Me-3)}C	NMe_2	H	2.489	2.320	0.169	181
				2.484	2.318	0.166	
2	{3-$R_3SiC_6H_3$}C	NMe_2	H	2.4732	2.3105	0.163	182
				2.4747	2.3154	0.159	
3	{3-$MeOC_6H_3$}C	NMe_2	H	2.472	2.341	0.131	183
4	{4-$MeOC_6H_3$}C	NMe_2	H	2.489	2.334	0.155	183
5	{5-$MeOC_6H_3$}C	NMe_2	H	2.466	2.338	0.128	183
				2.477	2.338	0.139	
6	{C_6H_4}C	NMe_2	Bu^t	2.466	2.341	0.125	184
				2.473	2.330	0.143	
7	{2-$C_{10}H_6$}C	NMe_2	Me	2.474	2.336	0.138	185
				2.465	2.338	0.149	
				2.487	2.336	0.129	
				2.474	2.334	0.140	
8	{1-$C_{10}H_6$}C [b]	NMe_2	Me	2.458	2.352	0.106	87
9	{1-$C_{10}H_6$}C [c]	NMe_2	Me	2.475	2.336	0.139	87
10	{(η^5-Cp)Fe(η^5-C_5H_3)}C	NMe_2	Me	2.477	2.325	0.152	186
11	{C_6H_4}C	$NHPr^i$	Me	2.493	2.331	0.162	187
				2.464	2.347	0.117	
		Average:		**2.475**	**2.333**	**0.142**	
				X = Br			
12	{C_6H_4}C	NMe_2	Me	2.584	2.465	0.119	185
				2.596	2.458	0.138	
13	{2-$C_{10}H_6$}C	NMe_2	Me	2.590	2.450	0.140	185
				2.599	2.450	0.149	
14	{C_6H_4}C	NHBn	H	2.580	2.430	0.150	188
				2.585	2.436	0.149	
15	{C_6H_4}C	NH_2	Me	2.447	2.332	0.115	189
				2.478	2.333	0.145	
		Average:		**2.557**	**2.419**	**0.138**	
				X = I			
16	{C_6H_4}C	NMe_2	Me	2.740	2.596	0.144	185
				2.745	2.596	0.149	
				X = OAc			
17	{C_6H_4}C	NBn_2	H	2.142	2.047	0.105	190
				2.127	2.048	0.114	
18	{C_6H_4}C [d]	NMe_2	H	2.174	2.072	0.102	27
				2.163	2.064	0.099	
19	{C_6H_4}C	NMe_2	COOMe	2.150	2.053	0.097	191
				2.146	2.052	0.094	
		Average:		**2.150**	**2.056**	**0.094**	
							
				X = Cl			
20	{CH_2CH_2}C	NMe_2	H	2.524	2.337	0.187	192
21	{$CMe_2CH(CHO)$}C	NMe_2	Me	2.476	2.334	0.142	193
		Average:		**2.500**	**2.335**	**0.165**	

Table 2 (continued).

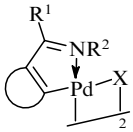
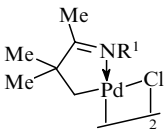
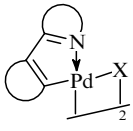
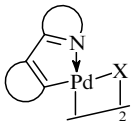
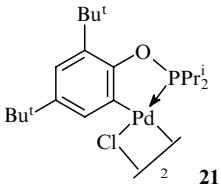
No.	Structure elements [a]		R^1	l(Pd – X) /Å		Δl /Å	Ref.
	C-Donor	N-Donor		*trans*-C	*trans*-N		
							
				X = Cl			
22	{C_6H_4}C	NBn	Bz	2.457	2.317	0.140	194
23	{C_6H_4}C	$NC_6H_3Me_2$-2,6	H	2.467	2.339	0.128	195
				2.452	2.331	0.121	
24	{(η^5-Cp)Fe(η^5-C_5H_3)}C	NTol-*p*	Me	2.469	2.331	0.138	196
				2.490	2.321	0.169	
25	{3-$MeOC_6H_3$}C	NCH_2pin [e]	H	2.462	2.340	0.122	197
				2.495	2.346	0.149	
		Average:		**2.469**	**2.330**	**0.139**	
				X = Br			
26	{3,4-$(MeO)_2C_6H_2$}C	NCy	H	2.565	2.439	0.126	198
27	{5-MeC_6H_3}C	NCy	H	2.598	2.447	0.151	199
				2.579	2.449	0.130	
28	{5-$MeOC_6H_3$}C	NCH_2pin	H	2.602	2.457	0.145	197
				2.564	2.454	0.110	
29	{(η^5-Cp)Fe(η^5-C_5H_3)}C	Nmmp [f]	Me	2.582	2.465	0.117	196
				2.601	2.437	0.164	
		Average:		**2.582**	**2.448**	**0.134**	
				X = OAc			
30	{C_6H_4}C	NAn [g]	Bz	2.141	2.054	0.087	200
				2.119	2.030	0.089	
31	{C_6H_4}C	NC_6H_4Cl-*p*	Bz	2.123	2.034	0.096	201
32	{4-$MeOC_6H_3$}C	NTol-*p*	H	2.139	2.026	0.113	202
33	{C_6H_4}C	NCy	Ph	2.166	2.041	0.125	203
34	{3-$MeOC_6H_3$}C	NCy	H	2.137	2.048	0.089	204
35	{4-$OCHC_6H_3$}C	NCy	H	2.146	2.041	0.105	205
				2.175	2.061	0.114	
				2.168	2.034	0.134	
				2.174	2.051	0.123	
36	{(η^5-Cp)Fe(η^5-C_5H_3)}C	NMes	H	2.153	2.042	0.111	206
				2.092	2.027	0.065	
37	{(η^5-Cp)Fe(η^5-C_5H_3)}C	NCH_2CO_2Et	H	2.137	2.036	0.101	207
				2.135	2.041	0.094	
		Average:		**2.143**	**2.040**	**0.103**	
							
38	{CMe_2CH_2}C	N{NPhMe}	NPhMe	2.490	2.334	0.156	208
39	{CMe_2CH_2}C	N{OH}	OH	2.546	2.341	0.205	209
		Average:		**2.518**	**2.338**	**0.180**	
							
				X = Cl			
40	{C_6H_4}C	N{4-Bu^t-ox} [h]		2.455	2.323	0.132	210
				2.470	2.320	0.150	
41	{C_6H_4}C	N{4-Ph-ox}		2.434	2.329	0.105	211
				2.472	2.323	0.143	
				2.433	2.312	0.160	
				2.466	2.341	0.092	
42	{C_6H_4}C	N{Py}		2.426	2.361	0.065	212
				2.434	2.366	0.068	
		Average:		**2.449**	**2.334**	**0.115**	

Table 2 (continued).

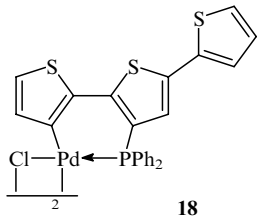
No.	Structure elements [a]		R[1]	*l*(Pd – X) /Å		Δ*l* /Å	Ref.
	C-Donor	N-Donor		*trans*-C	*trans*-N		
							
				X = I			
43	{(η^5-Cp)Fe(η^5-$C_5H_2SiMe_3$-3)}C [i]	N{4-($MeOCEt_2$)-ox}		2.738	2.587	0.151	213
44	{(η^5-Cp)Fe(η^5-$C_5H_2SiMe_3$-3)}C [j]	N{4-Bu^t-ox}		2.736	2.587	0.149	213
		Average:		**2.739**	**2.590**	**0.149**	
				X = OAc			
45	{C_6H_4}C	N{4,4-Me_2-ox}		2.125	2.049	0.076	214
				2.129	2.058	0.071	
46	{C_6H_4}C	N{4-Pr^i-ox}		2.124	2.061	0.063	215
				2.112	2.041	0.071	
				2.114	2.024	0.090	
				2.127	2.023	0.104	
				2.109	2.047	0.062	
				2.181	2.019	0.162	
				2.111	2.044	0.067	
				2.147	2.031	0.116	
47	{4-$NO_2C_6H_3$}C	N{Py}		2.14	2.03	0.11	216
48	{C_6H_4}C	N{im}		2.151	2.036	0.115	217
		Average:		**2.133**	**2.038**	**0.095**	

[a] The ligand fragment to which this donor atom belongs is given in braces. [b] *R,R-cis*-Isomer. [c] *R,S-trans*-Isomer. [d] The parameters for the μ-fluoroacetate dimer are given. [e] Here and below pin is pinan-3-yl. [f] mmp is 2-(methoxymethyl)pyrrolidine. [g] An is anisyl [h] Here and below, ox is oxazoline. [i] R_C,S_{pl}-Diastereomer. [j] S_C,R_{pl}-Diastereomer.

coordination of additional ligands to CN-palladacycles and account for the almost complete regioselectivity of these processes. Conversely, in the structures of dimeric CPC of the PC-type (see Table 1), the difference between the lengths of the two Pd – X bonds (X = Hal, RCOO) largely disappears: here the Δl_{av} values vary in the ranges of 0.010 – 0.058 and 0.007 – 0.037 Å for μ-halide and μ-carboxylate dimers, respectively. Moreover, for some complexes, the parameter Δ*l* decreases to negligibly low values (0.002 Å for dimer **21** [17]) or even changes the sign (−0.007 Å for dimer **18** [173]).

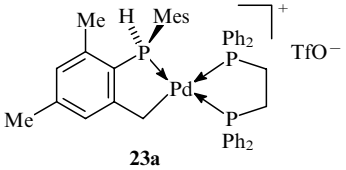


21

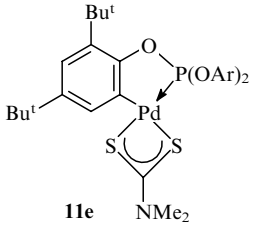


18

More evidence supporting the similarity of STE values of C- and P-donor atoms of phosphapalladacycles comes from the structural parameters of mononuclear derivatives of PC-palladacycles with symmetric ligands. In the cationic adduct **23a** [179] with the diphosphine ligand dppe, the lengths of two Pd – P bonds



23a



11e

Ar = $C_6H_3Bu^t_2$-2,4.

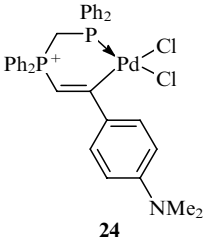
located in the *trans*-positions relative to the phosphapalladacycle C- and P-donor atoms differ only slightly (Δ*l* = 0.034 Å), and in the dithiocarbamate derivative **11e**,[69] the difference between the lengths of two Pd – S bonds does not exceed the experimental error (Δ*l* = 0.002 Å).

Analysis of these parameters entails quite a reasonable conclusion: the difference between the STEs of C- and P-donor atoms of phosphapalladacycles is too low to induce a satisfactory regioselectivity of their coordination to additional ligands. In most cases, one should expect a mixture of geometric isomers; the selective formation of one of these can rather be considered as an exception to the general rule.

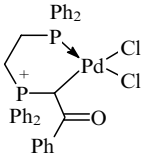
Comparative analysis of the dependence of the Pd – Hal bond length located in the *trans*-position relative to the PC-palladacycle carbon atom on the hybridisation of the C-donor atom leads to the conclusion that the *trans*-effect of the aliphatic carbon atom is higher than that for the aromatic atom. For example, in the structures of μ-chloride dimers of the PC type (see Table 1), the Pd – Cl bond lengths on the $C(sp^2)$ – Pd – Cl and $C(sp^3)$ – Pd – Cl diagonals vary in non-overlapping ranges 2.408 – 2.446 and 2.455 – 2.487 Å, respectively (the averaged l_{av} values are 2.429 and 2.472 Å, respectively, over 14 and 6 palladacycles). This trend is also retained in the structures of μ-bromide PC-dimers, although the available information is limited to only two structures. The Pd – Br bond lengths on the $C(sp^2)$ – Pd – Br and $C(sp^3)$ – Pd – Br diagonals in complexes **22** [177] and **3o** [176] are equal to 2.560 and 2.592 Å, respectively.

As was to be expected, the P-ylide carbon atom has the minimum STE. Indeed, in complexes **24** [180] and **15a**,[137] belonging to the common structural type [Pd(η^2-L)Cl_2], the Pd – Cl bonds located in the *trans*-position to the ylide carbon atom are 2.394 and 2.340 Å long, respectively, *i.e.*, they are substantially shorter than the average Pd – Cl bond lengths for the $C(sp^2)$ – Pd – Cl and $C(sp^3)$ – Pd – Cl diagonals in the classical μ-chloride PC-dimers (2.429 and 2.472 Å, respectively) and are below the lower limits of

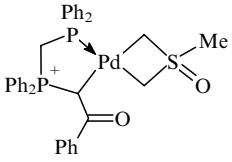
the ranges for these values (2.408 – 2.446 and 2.455 – 2.487 Å. respectively, see Table 1).



24



15a



16c

This result appears quite a natural consequence of the substantial delocalisation of the carbanion charge over both the phosphonium fragment and the electron-withdrawing substituents. Therefore, STE values of the C- and P-donor atoms in P-ylide complexes become comparable: the Δl value for two Pd – Cl bonds on the C – Pd – Cl and P – Pd – Cl diagonals is only 0.016 Å in complex **24** and becomes negative ($\Delta l = -0.050$ Å) in complex **15a**. The last-mentioned value shows that the STE of the P-donor substantially exceeds that for a σ-bonded carbon. This trend is retained for the bis(ylide) compound **16c**,[138] for which the parameter $\Delta l(\mathrm{Pd-C}) = -0.016$ Å attests to a greater *trans*-effect of the PPh_2 group compared to the P-ylide carbon.

Thus, using X-ray diffraction data, the C-donor phosphapalladacycles can be arranged in the following series in terms of increasing structural *trans*-effect: C(P-ylides) $\ll$ $C(sp^2)^-$ < $C(sp^3)^-$.

Unfortunately, the P-donor groups of various types cannot be classified legitimately in terms of their *trans*-effect relying on the Pd – X bond lengths available from X-ray diffraction data for dimeric complexes, due to both the scarcity of these data and too slight variations of this parameter (0.1 – 0.2 Å, see Table 1). As a preliminary estimate, one can consider the sequence of increasing STE for P-donors, which was derived from the averaged lengths of the Pd – Cl bond located in the *trans*-position to the P-donor atom of the phosphapalladacycle in μ-chloride dimers:

P-donor	C=P	$\leqslant$	$OP(OAr)_2$	$\leqslant$	$CPAr_2$	$\leqslant$	$CPAlk_2$	$\leqslant$	$OPAlk_2$
l(Pd – Cl) /Å	2.389		2.399		2.413		2.424		2.431

A greater *trans*-effect of the phosphinite phosphorus atom in OPR_2 compared to the phosphine atom is indicated by the decrease in the Pd – O bond length in μ-acetate dimers (see Table 1)

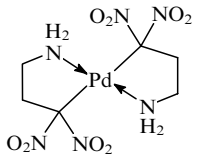
P-donor	$CPAr_2$	<	$OPAr_2$
l(Pd – O) /Å	2.117		2.143

Nevertheless, the need to elucidate more correctly the dependence of the STE of P-donors on both their chemical nature and the steric features of their environment is obvious. This requires detailed analysis of X-ray diffraction data for a broader range of phosphapalladacycle derivatives. At the current stage of research, it can only be stated that in most classical PC-palladacycles, the carbanionic centre exhibits a greater *trans*-effect, than the P-donor centre, no matter what is the carbon hybridisation (sp^2 or sp^3). However, in some classical PC-structures and in cyclopalladated derivatives of phosphino-P-ylides, the STE values of C- and P-donor atoms of a phosphapalladacycle are comparable, which implies a low regioselectivity of their reactions with auxiliary ligands.

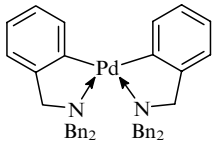
d. Manifestation of the transphobia in phosphapalladacycles

Analysis of the available data on the geometric configurations of various derivatives of PC-palladacycles largely confirms the above conclusions and demonstrates an essential difference between the PC- and CN-palladacycles.

***spiro*-Complexes**. In conformity with much more pronounced *trans*-effect of the carbanionic C-donor centres compared to hard N-donor centres, the vast majority of palladium [218 – 221] and platinum [221 – 227] bis(chelate) *spiro*-complexes with CN-type metallacycles exist as the *cis*(C,C)-configuration. Exceptions to this rule are scarce. The *trans*(C,C)-geometry of these complexes becomes possible only due to a sharp decrease in the difference between the STEs of the C- and N-donor atoms of the palladacycle. As an example, one can consider complex **25**,[228] in which the *trans*-effect of the carbanionic centre is sharply reduced due to the presence of two electron-withdrawing nitro groups, whereas the STE of the primary amino group is essentially higher than that of tertiary amino groups in analogous compounds (for example, in complex **26** [221]). As a consequence, the former complex exists as the *trans*(C,C)-isomer and the latter one has the standard *cis*(C,C)-geometry (the structures and configurations of both complexes were confirmed by X-ray diffraction).

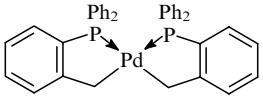


25

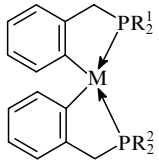


26

At first glance, an increase in the transphobia in the order C/P < C/C [111] would be sufficient for predicting the regiochemistry of formation of bis(chelate) *spiro*-complexes involving phosphapalladacycles. Indeed, two standard PC-palladacycles are usually combined into the *spiro*-structure in the *cis*(C,C)-configuration. This geometry exists both with the sp^3-hybridised carbanionic centre (for example, in complex **27** [229, 230]) and with the sp^2-hybridised carbanionic centre [for example, in complexes **2c** ¶ (see Ref. 71), **5b**,[71] **5e**,[71, 231 – 233] **5c** [71, 233] **28**.[71]]. The regiochemistry also does not depend on the nature of the substituent at the phosphorus atom, which may be either aromatic or aliphatic. Note that the *cis*(C,C)-configuration has been confirmed unambiguously by X-ray diffraction analysis. for platinum *spiro*-complexes **5′b**,[234] **2′c** [235] and **29′**.[222]



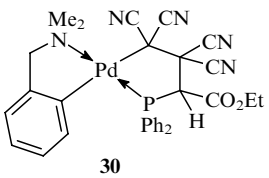
27



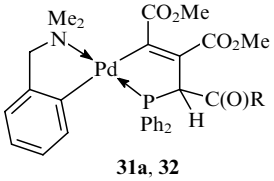
2c, **2′c**, **5b**,**c**,**e**, **5′b**, **28**, **29′**

M = Pd: $R^1 = R^2$ = Ph (**2c**), Bu^t (**5b**), Me (**28**);
R^1 = Bu^t: R^2 = Ph (**5e**), Me (**5c**);
M = Pt: $R^1 = R^2$ = Ph (**2′c**), Bu^t (**5′b**), Bn (**29′**).

However, analysis of the geometry of modified phosphapalladacyclic *spiro*-structures and conditions for their synthesis demonstrate that prohibition of the *trans*(C,C)-configuration is not very strict. For example, it does not apply to mixed-ligand *spiro*-complexes containing PC- and CN-palladacycles. Complex **30** with an alkyl [236] and complexes **31a** [237] and **32** [236] with an alkenyl C-donor in the phosphapalladacycle exist in solutions as *trans*(C,C)-isomers (the configuration of the former complex was determined by X-ray diffraction [236]).



30



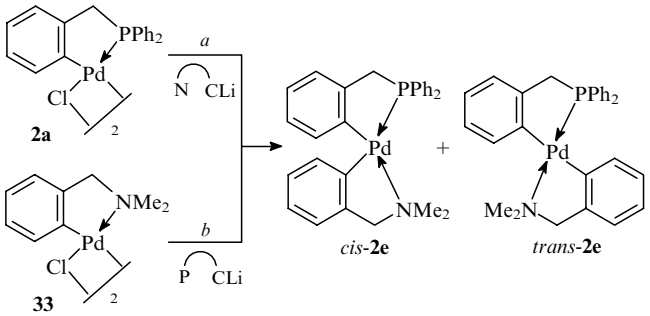
31a, **32**

R = Ph (**31a**), OEt (**32**)

¶ Early studies [232] assumed the formation of a mixture of *cis*- and *trans*-isomers of this complex.

The *trans*-configuration appears abnormal only from the standpoint of the classical view of the maximum STE for any carbanionic centre. However, the *trans*-effects of C(sp^3) in complex **30** and C(sp^2) in compounds **31a** and **32** are substantially reduced due to the presence of strong electron-acceptor nitrile or methoxycarbonyl groups. Under these conditions, the *trans*-effect of the phosphine PPh_2 fragment becomes more significant; as a result, the *cis*-localisation of this fragment relative to the phenyl carbon atom of the benzylaminate CN-palladacycle becomes quite justified from the standpoint of the transphobia concept.

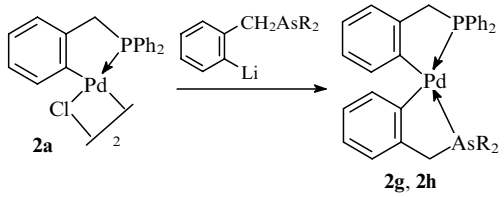
Yet another example of violation of classical rules is demonstrated by mixed-ligand complex **2e**, which is formed as a mixture of *cis*(C,C)- and *trans*(C,C)-isomers.[72,73] The structure of the predominant *cis*(C,C)-isomer has been confirmed by X-ray diffraction.[238] Probably, the dependence of the ratio of geometric isomers on the order in which the two palladacycles are closed is the most intriguing feature of this complex. Thus the formation of the CN-palladacycle on the PC-template (path *a*) results almost exclusively in the *cis*(C,C)-isomer, whereas the closure of the PC-palladacycle on the CN-template (path *b*) yields a mixture of *cis*(C,C)- and *trans*(C,C)-isomers, the former being the predominant product (~70%).[72,73]



cis : *trans* = 100 : 0 (*a*), 70 : 30 (*b*).

The formation of *trans*(C,C)-**2e** under conditions *b* was attributed to the possibility of system stabilisation due to a decrease in the electron density of the N-ligand (possessing strong σ-donor properties) by the *trans*-arranged P-donor atom. This explanation can hardly be accepted, because it implies the thermodynamic control of the process. Meanwhile, the differences between the two paths leading to the same complex are, most likely, due to changes in the reaction kinetics.

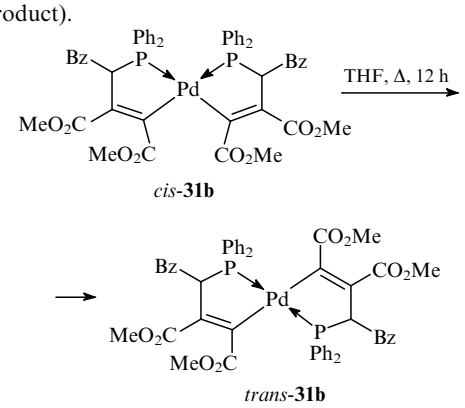
The dependence of the regiochemistry of the formation of *spiro*-complexes on the nature of the substituents in the heterodonor fragments has not been actually studied. One can only mention the results obtained in the synthesis of two mixed-ligand complexes containing simultaneously phospha- and arsenapalladacycles.[72] Closure of an AsC-palladacycle on a PC-template affords only the *cis*(C,C)-isomer if R = Ar (compound **2g**) or a mixture of *cis*- and *trans*-isomers (*spiro*-complex **2h**) if R = Alk (the isomer ratio has not been reported).



R = Ph (*cis*-**2g**), Me (*cis*/*trans*-**2h**).

The reasons for the difference between the regiochemistry of these two reactions have not been discussed in the study cited.[72] Since one can hardly expect a sharp increase in the STE upon the replacement of the $AsPh_2$ group by the more electron-enriched $AsMe_2$ fragment, it can only be assumed that either the geometry of the complexes is subject to the kinetic control or these systems do not obey the transphobia principle.

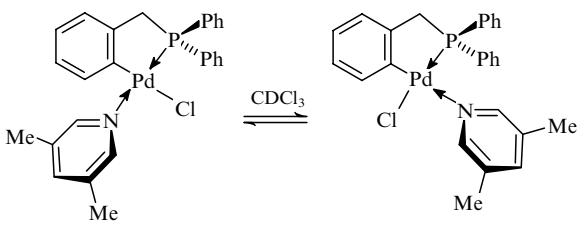
The behaviour of the alkenyl *spiro*-PC-complex **31b** should also be considered abnormal (from the standpoint of the transphobia concept).[237,239] This complex was obtained as the *cis*(C,C)-isomer (kinetically controlled product) under mild temperature conditions. However, the subsequent thermolysis of one diastereomer, *cis*(*R*,*S*)-**31b**, resulted in its quantitative conversion into the *trans*(C,C)-form (thermodynamically controlled product).



The structure and the configuration of both isomers, *cis*(*R*,*S*)-**31b**[239] and *trans*(C,C)-**31b**,[237] were confirmed by X-ray diffraction. These results provide a rare opportunity for estimating the relative STE of the P- and C-donor atoms in identical palladacycles. Similar Pd–P and Pd–C bond lengths in the two isomers prompted the conclusion[237] that the STEs of the phosphine and alkenyl groups are comparable. However, analysis of the variation dynamics of the bond lengths on passing from the P–Pd–C diagonal in the *cis*-isomer to the P–Pd–P and C–Pd–C diagonals in the *trans*-isomer shows that upon replacement of the *trans*-arranged vinylic carbon by a P-donor, the Pd–P bonds are elongated [Δl = 0.009(2) Å], whereas the reverse replacement resulted in shorter Pd–C bonds [Δl = −0.014(9) and −0.036(9) Å], the Δl values exceeding the experimental errors. These effects can be attributed to the greater STE of P-donor groups compared to the STE of the alkenyl carbon. However, the thermodynamic preference for the *trans*(C,C)-isomer cannot be explained in terms of the transphobia concept. Probably, in this case, steric effects make a significant contribution to the relative stability of the isomers.

Thus, even in the *spiro*-PC-complexes with two carbanionic C-donors (formally, possessing the highest *trans*-effect), the transphobia is not absolute, due to the insignificant difference between the STEs of the palladacycle C- and P-donor atoms.

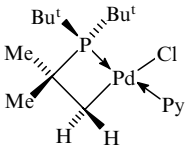
Adducts with N-donors. In the coordination of the phosphine PC-palladacycles with N-donor ligands, the degree of transphobia should be nearly the same for any geometry of the complex (C/Hal ~ C/N[153]); therefore, in this case, an isomer mixture is expected to form. The reaction of benzylphosphine dimer **2a** with 3,5-lutidine affords a 85 : 15 mixture of *trans*(N,P)- and *cis*(N,P)-isomers of adduct **2i**, which undergo fast (on the NMR time scale) interconversion in solutions at room temperature.[54]



Assuming that the STE of four ligands in complex **2i** varies in a sequence similar to that for platinum compounds

[$Ph^- > PPh_3 > Py > Cl^-$; NMR data (J_{Pt-P}) [158–160]], it is possible to explain the predominance of the *trans*(N,P)-isomer of adduct **2i** in which the softest (Ph^-) and the hardest (Cl^-) ligands are arranged on one diagonal.

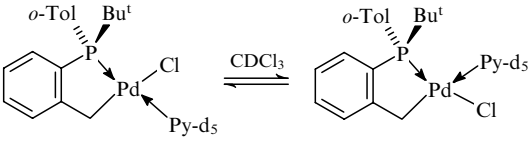
It has been assumed [88, 103] that the pyridine adduct **3p** with a four-membered PC-palladacycle exists only in the *trans*(N,P)-geometry.[88, 103] This assumption was based on the low frequency $\nu_{Pd-Cl} \approx 280\ cm^{-1}$ in the IR spectra and on the presence of only one signal in the ^{31}P spectrum and one set of signals in the ^1H NMR spectrum.



trans-(N,P)-**3p**

At a qualitative level, this is consistent with the STE scale. However, taking into account the change in the hybridisation of the carbon atom ($sp^2 \rightarrow sp^3$) and the increase in the basicity of the P atom, one could expect that the STE values for C- and P-donors would approach each other. Indeed, according to NMR data for platinum compounds (J_{Pt-P}), the following STE sequence was elucidated: $Ph^- > Me^- \geqslant PBu_3 > PPh_3 > Py > Cl$.[158–160] Therefore, in this case, the existence of two geometric isomers should rather be expected in solutions. The deviation of the experimental data from those predicted in terms of the transphobia principle may be due to a fast equilibrium between the isomers, because the Pd ← N bond in both isomers should be substantially weakened due to the σ-bonded carbon atom or the $PAlk_2$ group arranged on the same diagonal. The dynamic behaviour of the N-donor ligands is typical of PC-complexes. Their dissociation can be partly suppressed by introducing an excess of the incoming ligand.[60, 90] The spectra of these systems are more informative when recorded at low temperatures.[54]

The regiochemistry predicted in terms of the STE is supported by the spectroscopic detection of comparable amounts of *trans*(N,P)- and *cis*(N,P)-isomers (in 1 : 2 ratio) of the d_5-pyridine adduct **7e**, which belongs to the structural type characterised by the maximum STE for σ-C(sp^3)- and $PAlk_2$-donors.[90]



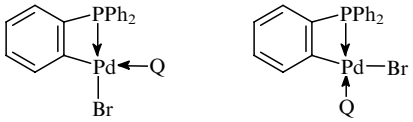
trans(N,P)-**7e** (1 : 2) *cis*(N,P)-**7e**

A reliable criterion for determining the geometry of these mononuclear adducts is provided by the opposite directions of shift of ^1H NMR signals for protons located most closely to the metallation site and belonging to P-substituents, caused by their moving towards the pyridine ring (shielding) or towards the halide ligand (deshielding). For example, in the spectrum of the *trans*-(N,P)-isomer of complex **7e**, the signal for the $PdCH_2$ methylene protons is shifted upfield ($\Delta\delta = -0.42$ ppm) with respect to its position in the spectrum of the *cis*(N,P)-isomer, whereas the signal for the PBu^t-group protons moves downfield ($\Delta\delta = +0.324$ ppm).[90] Under the optimal conditions, the difference between the chemical shifts of the same proton in the spectra of the two geometric isomers may reach 2 ppm.[145]

Adducts with P-donors. According to the transphobia concept, [152] monodentate phosphines should be more prone to *trans*-coordination relative to the P-donor atom of the phosphine PC-palladacycle (see Supplement 1) than N-donor ligands due to the pronounced destabilisation of the *trans*(P,C)-geometry. Indeed, the coordination of the sterically overcrowded phosphines, phosphites and phospholes to palladacycle **1c** based on trimesitylphosphine yields only *trans*(P,P)-isomers.[94] This is the only form for the triphenylphosphine adducts of cyclopalladated α-ferrocenylalkylphosphines **9b** and **10b**.[78, 79]

However, as opposed to CN-systems, the coordination of phosphines to phosphapalladacycles is not absolutely *trans*(P,P)-selective. The phosphine adducts formed by sterically non-hindered palladacycles are often formed as mixtures of *cis*- and *trans*-isomers with pronounced predominance of the latter. The recent repeated investigation of cyclopalladated di(*o*-tolyl)-*tert*-butylphosphine (HL^7) has shown that its triphenylphosphine adduct exists as a mixture of *trans*- and *cis*-isomers (12 : 1).[117] The fact that only the *trans*-isomer was previously identified for this complex by spectroscopy [60] suggests that other non-selective systems of this type may also exist.

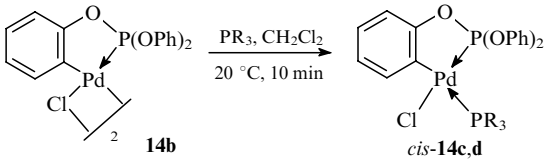
The essential deviations of the configuration of complexes from those predicted on the basis of the transphobia concept arise upon modification of the nature of the C- or P-donor centres of the palladacycle or its size. For example, the phosphine adducts of the *ortho*-palladated triphenylphosphine with a strained four-membered palladacycle are formed as mixtures of geometric isomers whose ratio varies over a broad range depending on the structure of the phosphine used.[240, 241]



cis-**34a**,**b** *trans*-**34a**,**b**

Q = $PPh_2(C_6H_4Cl\text{-}o)$ (**34a**), $P(Tol\text{-}p)_3$ (**34b**);
cis : *trans* = 93 : 7 (**a**), 20 : 80 (**b**).

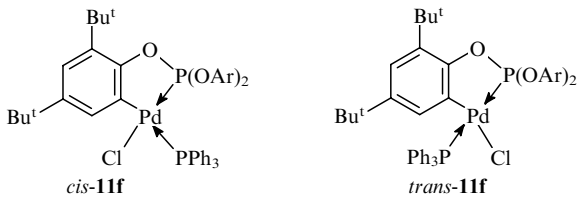
The regiochemistry of coordination of P-donor ligands to cyclopalladated derivatives of substrates having enhanced π-acidity depends on the electronic characteristics of the ligands and on the steric situation in the coordination sphere. Most triaryl phosphite- [58, 69, 74, 242] and arylphosphinite-based [115] CPCs bind monodentate phosphines and phosphites, preferably in the *cis*(P,P)-geometry (for example, complexes **14c**,**d**, see Supplement 1). This unusual fact may be explained by the clearly pronounced π-acceptor nature of the phosphorus atom in the phosphite palladacycle,[101] which accounts for system destabilisation upon *trans*-coordination of monodentate π-acceptor phosphites or phosphines.



14b *cis*-**14c**,**d**

R = Ph (**14c**, 96%), MeO (**14d**, 89%).

However, in the case of sterically crowded dimer **11a**, the *cis*(P,P)-regiospecificity is retained only in reactions with monodentate phosphites $P(OR)_3$ (R = Me, Et, Ph),[69] while on passing to phosphine auxiliary ligands, the formation of the *trans*(P,P)-isomer also becomes possible. For example dimer **11a** reacts with PPh_3 to give a mixture of *cis*(P,P)- and *trans*(P,P)-isomers **11f**, the latter being the major product (ratio 1 : 2.4).[69]

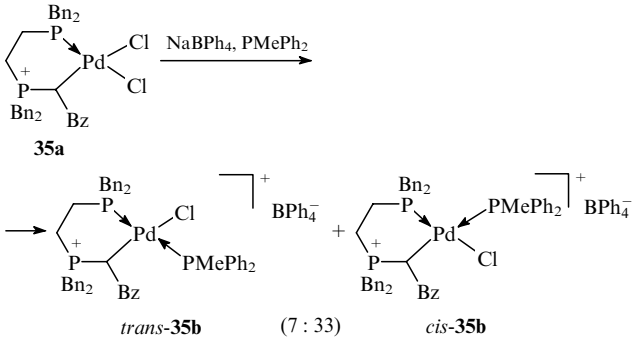


cis-**11f** *trans*-**11f**

Ar = $C_6H_3Bu^t_2$-2,4.

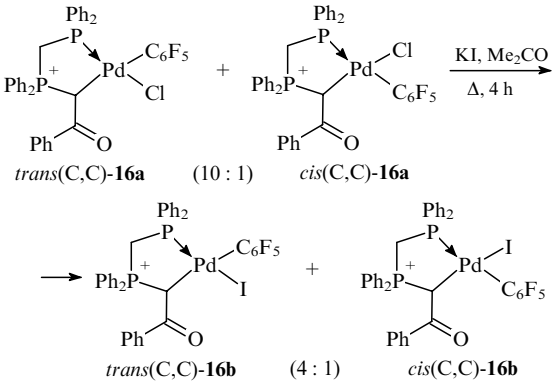
The formation of an isomer mixture has also been detected in reactions of dimer **11a** with PCy_3 (under certain conditions).[69] In this case, the tendency for the formation of *trans*(P,P)-isomers of the phosphine (but not phosphite) adducts may be due to steric effects. Indeed, phosphines PR_3 have a greater bulk than phosphites $P(OR)_3$ with the same groups. For example, the Tolman cone angles θ for the phosphines PPh_3 and PCy_3 are 145 and 179°, while for the similar phosphites $P(OPh)_3$ and $P(OPr^i)_3$, these angles amount to 121 and 114°, respectively.[95,243] Therefore, the coordination of phosphines in the *cis*-position relative to the bulky $P(OAr)_2$ fragment of dimer **11a** should be sterically hampered.

One more example of abnormal regioselectivity is the formation of phosphine derivatives of phosphino-P-ylide palladacycles. The replacement of the carbanion C-centre in cyclopalladated phosphines by an ylide centre (*i.e.*, bearing only a partial negative charge) results in a decrease in its *trans*-effect compared to the STE of the P-donor atom (see Section II.2.c). Under these conditions, one should expect an inverted regiochemistry of the coordination of auxiliary ligands. Indeed, the reaction of dichloride **35a** with phosphine $PMePh_2$ yields a mixture of *trans*(P,P)- and *cis*(P,P)-isomers of cationic complex **35b**, the latter being the predominant product.[136]



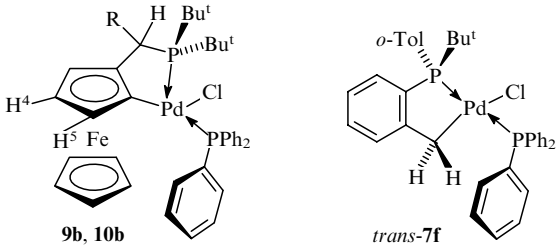
The preference of the *trans*-coordination of phosphine $PMePh_2$ relative to the ylide carbon atom is even more pronounced in its reaction with similar dichloride **15a**; in this case, the *trans*(P,P)- and *cis*(P,P)-isomer ratio for the cationic complex $[Pd(\eta^2\text{-}L^{15})Cl(PMePh_2)]BPh_4$ (**15i**) increases to 1 : 7.[132]

The reduced STE of the ylide carbon can also be illustrated by the preferred formation of the *trans*-(C,C)-isomers of monoarylated derivatives of phosphino-P-ylide palladacycles (this contradicts the formal prediction based on the transphobia concept[111,113,152]). In structures of this type (for example, in complex **16a**), the *trans*(C,C)- to *cis*(C,C)-isomer ratio varies over a rather broad range. In chloride complexes, it varies from 3 : 1 to 10 : 1. The content of the *cis*(C,C)-isomer increases when the chloride in complex **16a** is replaced by softer iodide (complex **16b**).[133]



The magnitudes of the spin–spin coupling of two phosphorus nuclei may serve as a reliable criterion for estimating the geometric configuration of the adducts of various PC-palladacycles with P-donor ligands.[244] In the adducts of phosphine- and phosphinite-based PC-palladacycles with phosphines having the *trans*(P,P)-configuration, the $^2J_{PP}$ values vary in the range of 360–441 Hz. The $^2J_{PP}$ values increase to 604–607 Hz when a phosphite phosphorus atom appears in either the palladacycle[69] or the auxiliary ligand[94] (see Supplement 1). In complexes having the *cis*(P,P)-geometry, this parameter decreases by more than an order of magnitude ($^2J_{PP}$ = 19–56 Hz). The legitimacy of this criterion is confirmed by the fact that in the mononuclear derivatives of PC-palladacycles with diphosphines, the coupling constants between the ^{31}P nucleus of the metallacycle and diphosphine phosphorus nuclei located in the *trans* and *cis* positions vary approximately in the same ranges ($^2J_{PP}$ = 333–540 and 30–52 Hz, respectively).[30,58,69,115]

The ^1H NMR spectra provide less unambiguous information on the geometric configuration of the coordination sphere of the PC-palladacycle adducts with P-donor ligands. The *trans*(P,P)-geometry of the phosphine adducts of the classical PC-palladacycles (with the phosphine donor atom) can be confirmed by shielding of the PC-palladacycle proton located most closely to the metallation site by the P-aryl groups of the auxiliary ligand.[78,79,90] For example, the ^1H NMR spectra of the PPh_3-adducts **9b**[79] and **10b**[78] show the signal for the H^5 proton of the palladated cyclopentadienyl fragment shifted upfield by $\Delta\delta$ = 1.18 and 0.92 ppm, respectively, with respect to its position in the spectra of the (*S*)-prolinate derivatives of the same palladacycles.[90] This effect is less pronounced in compounds with the $C(sp^3)-Pd$ bond. For example, in the spectrum of adduct **7f**, the $\Delta\delta$ value for the $PdCH_2$-protons in the *trans*(P,P)-isomer is only 0.33 ppm.[117]

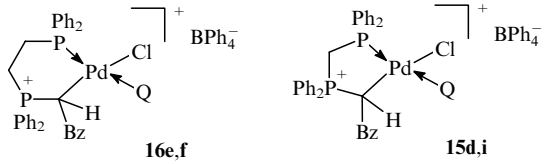


R = H (**9b**), Me (**10b**)

The idea of using, for diagnostic purposes, the direct through-space coupling of the proton nearest to the metallation site with the phosphorus nucleus seems attractive at first glance. However, this criterion should be used with caution. In the case of PC-palladacycle derivatives, the situation is complicated by the presence of two ^{31}P nuclei, whose effects are to be differentiated. For example, in the ^1H NMR spectrum of the *trans*(P,P)-isomer of complex **7f**, the diastereotopic protons of the $Pd-CH_2$ fragment are coupled with both the PPh_3 ligand ($^3J_{HP}$ = 11.0 and 5.7 Hz) and the ^{31}P nucleus of the phosphapalladacycle ($^3J_{HP}$ = 3.7 and 2.8 Hz).[117] Since both phosphorus atoms are separated from the $PdCH_2$-protons by three bonds, it seemed justified to assign the much greater spin–spin coupling constants of these protons with the phosphine PPh_3 to an additional contribution of the through-space coupling of these nuclei. However, the use of this criterion is complicated, first, by the dependence of the coupling constant on the geometry and the nature of bonds separating the nuclei and, second, by the possibility of spin–spin coupling through rather long bond sequences. For example, the spectrum of the complex **9b** mentioned above was found to exhibit quite a detectable constant $^5J_{HP}$ = 0.5 Hz (through five bonds!) for the remote H^4 proton of the palladated cyclopentadienyl fragment.[79]

The ^1H NMR-based criteria proved inapplicable to phosphino-P-ylide analogues. Indeed, a comparison of the chemical shifts of the ylide CH proton in the spectra of the starting dichlorides **15a**, **16d** (δ = 6.05–6.01 ppm)[129,134] and their adducts with the phosphines PCy_3 and PPh_3[131,132] shows that the upfield shift of this signal is more pronounced for complexes

with the aliphatic phosphine (δ = 4.02–4.47 ppm for **15i**, **16f**) than with the aromatic one (δ = 4.54–4.90 ppm for **15d**, **16e**).

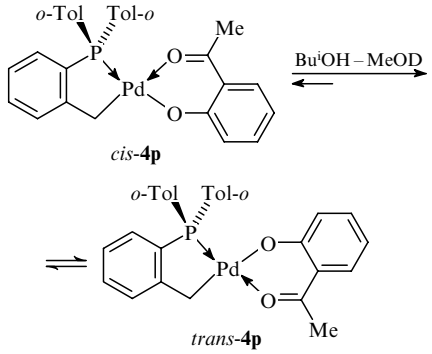


16e,**f** **15d**,**i**

Q = PPh_3 (**15d**, **16e**), PCy_3 (**15i**, **16f**).

The researchers cited assume that this shift is due to either shielding of the ylide proton by the phosphorus nucleus [131] or by the increase in the electron density on the metallic centre upon the introduction of phosphine ligands.[132] The latter version seems more likely in view of the much higher basicity of the aliphatic phosphine compared to the aromatic phosphine (for PCy_3 and PPh_3, pK_a = 9.70 and 2.73, respectively [101]).

An example of low regioselectivity of coordination of non-symmetric bidentate ligands is provided by 2-acylphenolate derivatives of dimer **4a**, which are formed as mixtures of *cis*- and *trans*-isomers.[118] The researchers were able to increase the regioselectivity by varying the solvent. For example, complex **4p** exists as only the *trans*-isomer in a Bu^iOH–MeOD mixture, whereas in CCl_4, d_8-toluene, C_6D_6, d_6-DMSO and $CDCl_3$, the *cis* : *trans* ratio varies from 1 : 2 to 1 : 9.[118]



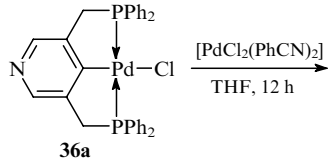
cis-**4p**

trans-**4p**

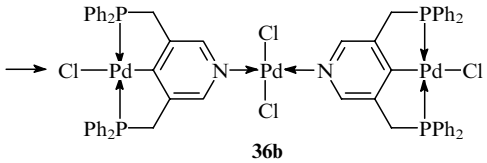
In conclusion, we would like to note that the transphobia concept,[111, 113, 152] which describes rather adequately the behaviour of CN-palladacycles with respect to Lewis bases, is far from being always applicable to their PC-analogues as the reaction regiochemistry is strongly dependent on the electronic and steric factors. The predictive potential of this concept would be essentially increased by elucidation of detailed and correct *trans*-effect sequences for cyclopalladated compounds differentiated according to the types of P- and C-donors.

3. Bicyclic PCP-complexes

The derivatives of bicyclic PCP-systems are less diverse, because the possibility of their modification is usually restricted to one coordination site. Probably, the 'pincer' compound **36a** with the pyridine core, which can function as a metalloligand due to the pyridine nitrogen atom, is the only exception to this rule. For example, the reaction of this compound with palladium(II) benzonitrile complex affords trinuclear compound **36b** with two PCP fragments at the periphery.[245]



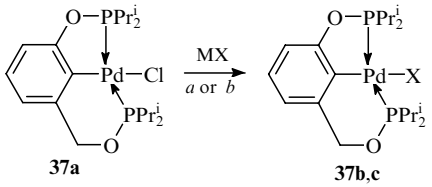
36a



36b

This method for aggregation of cyclometallated complexes may be useful for the design of multicentre polynuclear catalysts.

The standard initial form of PCP-complexs is a monomer with anionic ligand (Hal^- or $RCOO^-$). The exchange of these anions opens up the way to other derivatives. For example, chloride complex **37a**, prepared recently by direct cyclopalladation of non-symmetrical bis(phosphinite) HL[37] by [$PdCl_2$(cod)] (cod is cycloocta-1,5-diene), was converted into iodide (**37b**) and acetate (**37c**) analogues.[246]

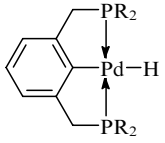


37a **37b**,**c**

M = Na, Ag; X = I (**37b**), AcO (**37c**);
(*a*) NaI, Me_2CO; (*b*) AgOAc, Et_2O, ultrasound.

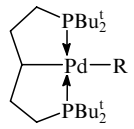
To replace chloride by the softer iodide, complex **37a** should be merely treated with NaI, whereas the replacement of the chloride by harder acetate requires dehalogenation of the initial chloride complex on treatment with AgOAc with ultrasonic activation.

The reactivity of PCP-complexes differs somewhat from that of their monocyclic PC-analogues. The formation of stable hydride derivatives (which are unknown for PC-structures) is the most interesting feature. The mononuclear hydrides, for example, **38a** [247] and **39a**,[248] are prepared by treating the chloride precursors with hydride reagents ($NaBH_4$ or $LiAlH_4$), while the quantitative formation of binuclear hydride **40a** is attained by elimination of the chloride by the action of AgOTf followed by introduction of sodium formate.[249, 250]



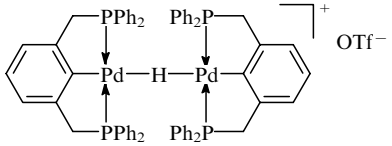
38a, **40b**

R = Bu^t (**38a**), Ph (**40b**)



39a,**b**

R = H (**39a**), Me (**39b**)



40a

Presumably,[250] the stability of the PCP-complexes with the Pd–H bond unusual for hydrides is determined by efficient shielding of this bond by bulky PBu^t_2 groups. This is consistent with both the higher stability of binuclear hydrides (in which the Pd–H–Pd fragment is not destroyed even under the action of CO or alkenes [249]) compared to the mononuclear ones and the lower stability of mononuclear CPC hydride derivatives based on sterically non-hindered diphosphines. For example, the formation of hydride **40b** from the PCP-complex with PPh_2 groups (through β-H elimination from the amide derivative) has been detected only by spectroscopy, whereas on attempted isolation, it was converted

into more stable binuclear complex **40a** with the bridging hydride ligand.[251] Conversely, mononuclear hydride **39a** with bulky Bu^t substituents at the phosphorus atoms does not decompose even on heating above 100 °C.[248]

Probably, it is due to the low steric protection of the Pd—H bond in binuclear hydride **40a** that this hydride is easily converted into the chloride [Pd(η^3-L^{40})Cl] (**40c**). This was the case, for example, on attempted crystallisation of complex **40a** as the BPh_4 salt from a solvent mixture including dichloromethane.[252]

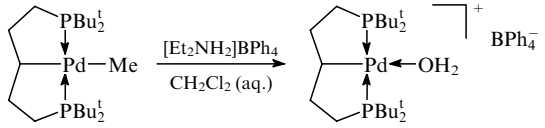
Derivatives of PCP-complexes with molecular hydrogen like [(η^3-L)Pd(η^2-H_2)]$^+$ might be of interest for the use in catalytic hydrogenation. However, attempts to generate such species by protonation of hydride **38a** with acids such as TfOH, $HBF_4 \cdot OEt_2$ or [H(OEt_2)$_2$]BAr_4 have not met with success.[253] Note for comparison that platinum analogues have been detected by spectroscopy at low temperatures.[254]

The replacement of the chloride in PCP-complexes by a methyl group on treatment with MeLi is a route to convenient catalyst precursors. Protolysis of these methyl derivatives [255] (for example, on treatment of complex **39b** with the salt [Me_3NH]BF_4 [248]) yields active coordinatively unsaturated species capable of functioning in a catalytic cycle by binding either the substrate or the reagent. These species can also be generated by dehalogenation of appropriate chloride PCP-complexes with $AgBF_4$ or $TlPF_6$.[256] The coordination vacancy is usually occupied by a solvent molecule (THF, dioxane, acetone, CH_2Cl_2, $CDCl_3$);[256] weak binding of the anion is also possible:[248]

$$[(PCP)Pd(solv)]^+ BF_4^- \longleftrightarrow [(PCP)Pd(FBF_3)].$$

When solvated, PCP-complexes are most convenient for the preparation or generation *in situ* of the adducts with weakly coordinated neutral monodentate ligands. The stability of these cationic adducts depends to a large extent on electronic and steric characteristics of both the PCP-template and the ligand entering the metal coordination sphere.

For example, the solvated derivative of PCP-template **39** with bulky PBu^t_2 groups generated *in situ* by the protolysis of Me-substituted complex **39b** proved incapable of forming adducts with secondary and tertiary amines (Et_2NH, Me_3N).[248] In particular, the reaction of compound **39b** with the ammonium salt [Et_2NH_2]BPh_4 (this reagent performed a dual function, being a protonating agent and a potential source of the amine ligand) in moist dichloromethane gave aqua complex **39c**, whose structure was confirmed by X-ray diffraction, instead of the expected adduct with the amine.[248]

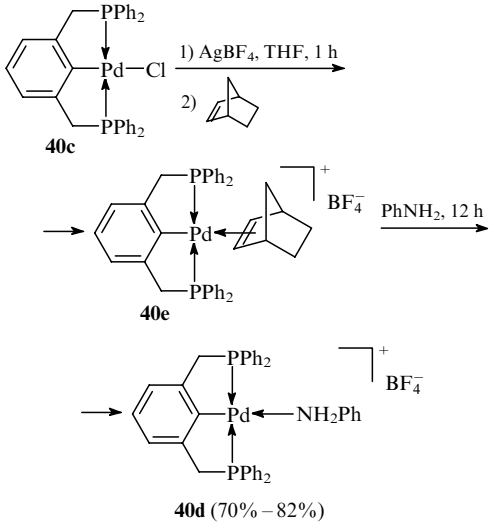


39b **39c**

The researchers attributed this outcome to blocking of the newly formed coordination vacancy by bulky PBu^t_2 donor groups of the PCP-template [248] (apparently, some contribution is made by relatively high steric requirements of the amines Et_2NH and Me_3N, for which θ = 125 and 132°, respectively [257]).

Conversely, complex **40c** with less bulky Ph_2P donor groups forms an adduct with Me_2NH,[251, 258] apparently, owing to the less pronounced steric restrictions from both the PCP-core and the amine. After deprotonation of the secondary amine incorporated in [Pd(η^3-L^{40})(NHMe$_2$)]OTf, the amide derivative [Pd(η^3-L^{40})(NMe$_2$)],[251] an analogue of an intermediate involved in palladium-catalysed amination, has been detected by spectroscopy.[13]

The coordination of the PCP template **40** with aniline is also facilitated by both factors: the lower steric requirements of the PCP-fragment and the relatively small size of the amine (aniline) (θ = 111°).[257] Complex **40d** was prepared in a high yield upon the substitution of aniline for norbornene (nb) in the intermediate adduct [Pd(η^3-L^{40})(η^2-nb)]BF_4 (**40e**) generated *in situ* from chloride **40c**. The structure of complex **40d** was confirmed by X-ray diffraction.[256]

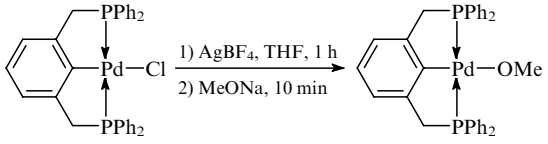


40c

40e

40d (70% – 82%)

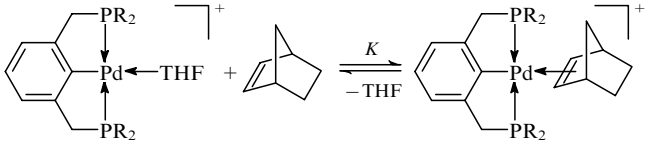
Within the framework of the same study devoted to the simulation of transformations like the Wacker process, hydroxy and some alkoxy derivatives of complex **40c** were synthesised and characterised by spectroscopy.[256] Thus dehalognation of chloride **40c** with the subsequent introduction of sodium methoxide gave methoxide **40f**.[256]



40c **40f**

Undoubtedly, a substantial contribution to weakening of the palladium bond with the incoming monodentate ligand is made by the strong *trans*-effect of the carbanionic centre of the PCP-template located opposite to this ligand. As an illustration, one can consider the protolytic displacement of the relatively small aliphatic phosphine PEt_3 (θ = 132°) from the complex [Pd(η^3L^{40})(PEt_3)]BF_4 (**40g**) with the sterically non-hindered template. The structure of adduct **40g** was confirmed by X-ray diffraction.[259] The displacement of the phosphine from the coordination sphere is attained by mere treatment of complex **40g** with a 0.1 M solution of HBF_4 in MeCN. The initial CPC can be regenerated as the acetonitrile solvate. It is significant that the attempts to displace PEt_3 from its adducts with PNP-, PSP- and POP-templates containing the central heterodonor atom failed.

The possibility of the electronic control of the complexation of PCP-templates with additional ligands is illustrated by the results of a study dealing with norbornene binding to two complexes differing by the P-substituents. Adducts **40e** and **41b** have not been isolated due to the substantial weakening of alkene coordination, caused by the pronounced *trans*-effect of the carbanion centre of the PCP-template, but they have been identified by spectroscopy. Determination of the equilibrium constants between the starting solvates **40h**, **41a** and their norbornene adducts **40e**, **41b** showed



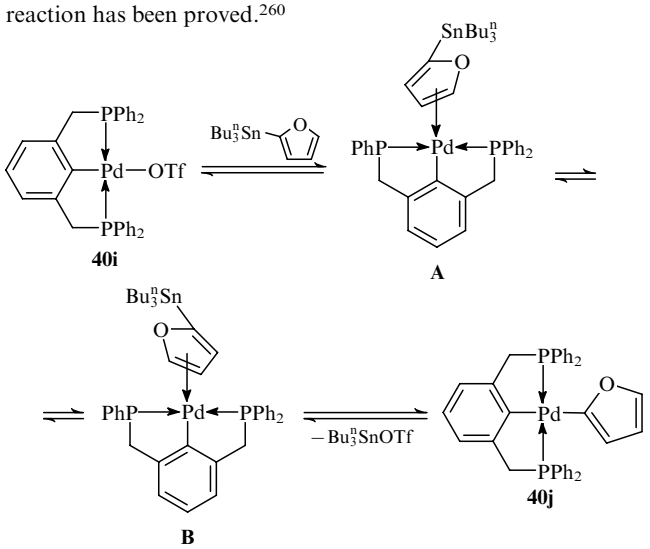
40h, **41a** **40e**, **41b**

R = Ph (**40h**,**e**; K = 0.17), 4-$Me_2NC_6H_4$ (**41a**,**b**; K = 0.41).

that binding of the bicyclic alkene becomes stronger upon the introduction of the electron-donor Me_2N substituents into the benzene rings of the template PPh_2 groups.[256]

The high stability of the alkene adduct **41b** is attributed to the increase in the electron density on the metal (the effect is transmitted from the heterodonor PAr_2 groups), resulting in a greater contribution of the back d-π-backbonding of the metal to the alkene.[256]

The above examples clearly demonstrate the good prospects for the use of PCP-structures for stoichiometric simulation of the intermediates in the catalytic processes. This becomes possible due to the exceptionally high stability of this type of CPC, caused by the efficient steric shielding of the reaction centre. Using PCP-complex **40i** as the catalyst, the intermediates in the Stille coupling have been identified and the Pd^{II}/Pd^{IV} route of this catalytic reaction has been proved.[260]



The hetarylation product of catalyst **40i** with α-stannylfuran, complex **40j**, has been not only isolated but also studied by X-ray diffraction. The intermediate with a η^2-coordinated organotin reagent existing as two isomers **A** and **B**, which directly precedes complex **40j** in the catalytic cycle, has been identified by low-temperature spectroscopy. The structure and stereochemistry of complexes **A** and **B** in solutions were convincingly proved by the whole set of advanced spectral methods (^1H, ^{31}P, ^{119}Sn NMR) including the NOE technique (Nuclear Overhauser Effect).

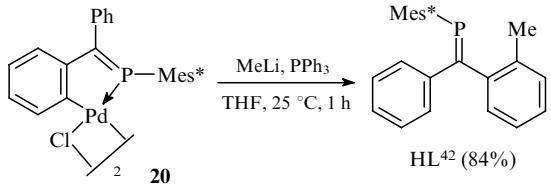
As a result, the sequence of reversible stages of this process was established and the thermodynamic parameters for substrate η^2-coordination and transmetallation were determined.[260]

III. Transformations of phosphapalladacycles

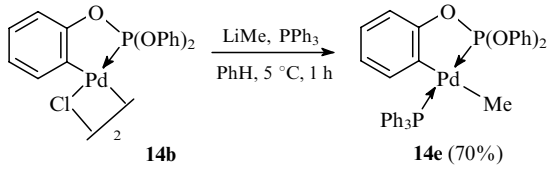
We have discussed so far the reactions that involved the metallic centre but left the phosphapalladacycles intact, only the metal coordination environment being varied due to the introduction of auxiliary ligands. This Section deals with processes affecting the metal-containing rings. These can be divided into three types: (1) reactions at the Pd—C bond of the palladacycle, which allow regioselective introduction of substituents into the initial P-containing ligand (Section III.1); (2) structural modification of the phosphapalladacycle not affecting the Pd—C and Pd—P bonds (Section III.2); (3) dechelation and destruction of PC-palladacycles (Section III.3).

1. Reactions of phosphapalladacycles involving the Pd—C bond

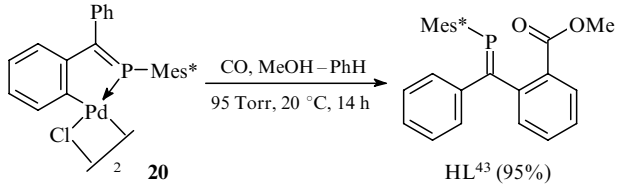
The reactions of phosphapalladacycles involving the Pd—C bond are of considerable interest as a method for regioselective modification of the P-donor ligands. Unlike CN-palladacycles for which these reactions have been extensively studied within the framework of development of the routes of regioselective organic synthesis,[261–265] studies of the transformations of PC-palladacycles are limited to a few examples. Of the few known publications, a brief communication dealing with the reactions of cyclopalladated phosphaalkenes with some nucleophiles deserves attention.[86] Thus by treating the dimeric complex **20** with an organolithium reagent in the presence of triphenylphosphine, the *ortho*-methylated analogue of the initial ligand HL[20], phosphaalkene HL[42], has been obtained.



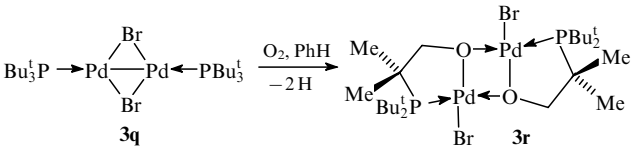
When MeLi was replaced by Bu^nLi or PhLi, the product yield markedly decreased and alkylation with more bulky Bu^tLi proved impossible at all (apparently, due to steric restrictions). It should be noted that an attempt to obtain *ortho*-substituted phosphites failed: in this case, the reaction stopped after replacement of the chloride in the intermediate phosphine adduct [Pd(η^2-L)(PPh_3)Cl] by the organic ligand R. For example, dimer **14b** is converted into mononuclear complex **14e** under these conditions.[74]



The carbonylation of the phosphaalkene complex **20** at room temperature but at high CO pressure gave new ligand HL[43], containing a methoxycarbonyl group in the *ortho*-position of one benzene ring, in an almost quantitative yield.[86]



Two other examples of reactions involving the Pd—C bond refer to transformations of strained four-membered PC-palladacycles. The oxidation of dimeric Pd(I) complex **3q** with atmospheric oxygen affords binuclear Pd(II) complex **3r** with a new phosphino-alcoholate ligand.[176]

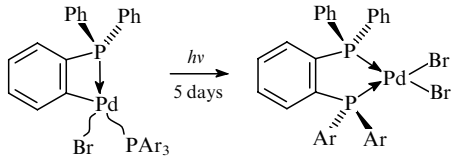


In view of the ease of cyclopalladation of tris(*tert*-butyl)phosphine,[12] participation of a cyclopalladated intermediate in the oxidation of complex **3q** seems quite practicable, the more so, because a small amount of the dimeric CPC [{(η^2-L^3)Pd(μ-Br)}$_2$] (**3o**) has been isolated from the reaction mixture. Presumably, this process includes coordination of the oxygen molecule, cleavage of the metal-activated O=O bond, cyclopalladation of the phosphines and the subsequent formal insertion of oxygen into the resulting Pd—C bond. The structures of both the final product **3r** and intermediate dimer **3o** were proved by X-ray diffraction analysis.[176]

It is noteworthy that the μ-iodide analogue of complex **3q** was absolutely inert with respect to atmospheric oxygen. The depend-

ence of the ability of compounds of this class to undergo oxidative addition on the nature of the halide (Br ≫ I) has also been noted for their reactions with other small molecules (CO, H_2, RCN).[176]

A more practically interesting process has been discovered in a study of the behaviour of phosphine adduct **34c**, containing sterically strained four-membered PC-palladacycle, under photochemical activation.[266] A mixture of *cis*- and *trans*-isomers of this complex in the solid state is converted in the light at room temperature into coordination compound **44a** with *o*-phenylenediphosphine, formed upon the formal insertion of the PPh_2 group into the Pd–C bond. The fact that the second phosphine fragment PPh_2 is formed from the phosphine PPh_3, bound in the monodentate mode in the initial complex **34c**, was confirmed by experiments with deuterated (Ar = C_6D_6, complex **34d**) and structurally modified (Ar = Tol-*p*, complex **34e**) analogues of adduct **34c**. The structure of one product of this unusual reaction, complex **44a**, was proved by X-ray diffraction.

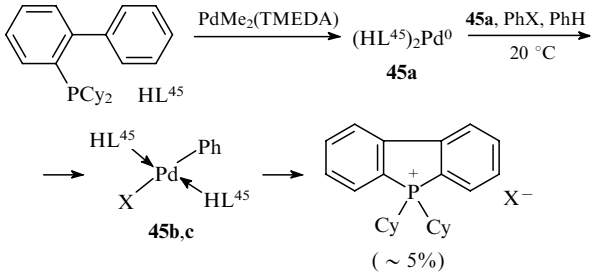


34c–e **44a–c**

Ar = Ph (**34c**, **44a**), C_6D_5 (**34d**, **44b**), Tol-*p* (**34e**, **44c**).

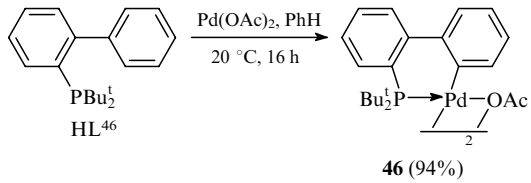
Apparently, the formation of the P–C bond may be either an inter- or an intramolecular process. A study of the reactions of aryl halides with Pd(0) complex **45a** containing bulky phosphine ligands HL^{45} has shown the formation (in addition to the standard oxidative addition products **45b**,**c**) of a small amount (~5%) of cyclic phosphonium salts.[267]

The structures of complex **45a** and two phosphonium salts with $X^- = Br^-$ and I^- were confirmed by X-ray diffraction. When discussing the origin of these salts, the authors reasonably suggest that they result from metallation of the *ortho*-carbon atom in the remote benzene ring of the biphenylphosphine HL^{45} followed by reductive elimination of the P–C bond in the intermediate phosphapalladacycle.



X = Br (**45b**), I (**45c**); TMEDA — $Me_2N(CH_2)_2NMe_2$.

This reaction route is supported by a number of considerations. First, a similar six-membered phosphapalladacycle **46** has been obtained recently in an almost quantitative yield under mild conditions.[18]

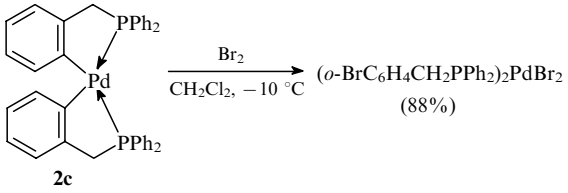


46 (94%)

Second, X-ray diffraction and spectroscopic studies of the Pd(0)-containing starting complex **45a** has revealed π-coordination of the metal to the remote benzene ring of biphenylphosphine, which is usually considered as an initial step of cyclometallation.[12] Presumably, interactions of this type are also possible in complexes **45b**,**c**, containing Pd(II). Finally, the presence of the Ph–Pd fragment in intermediate complexes **45b**,**c** should largely facilitate the cyclometallation.[12]

Note for comparison that the intermolecular formal insertion of the PR^1R^2 fragments into the Pd–C bond of more stable five-membered CN-palladacycles has been carried out only using lithium phosphides $LiPR^1R^2$ (Refs 268–270) or $PhPCl_2$.[271]

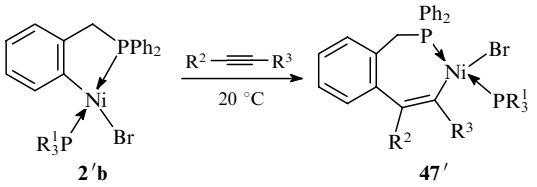
Studies of the reactivity of bis(chelate) *spiro*-PC-complexes of benzylphosphines have shown that their reactions with bromine result in the destruction of the phosphapalladacycle through the formal insertion of bromine into the Pd–C bond. This gave coordination complexes of palladium bromide with *ortho*-brominated phosphines in high yields.[67]



2c

A practical significance of this process is problematic, because *o*-bromobenzylphosphines formed serve as the starting substrates for the synthesis of *ortho*-lithiated ligands (in particular, LiL^2), necessary for the preparation of *spiro*-complexes. Note for comparison that analogous platinum(II) compounds undergo oxidative addition under these conditions with retention of the phosphametallacycle in the intermediate platinum(IV) complexes of the type $[(P^\frown C)_2PtBr_2]$.[67, 71]

Strange as it seems, reactions of phosphapalladacycles with alkynes have not yet been studied, although this line of research is being developed most extensively in the chemistry of CN-analogues.[263, 264] The possibility of these reactions for PC-complexes is supported by their implementation for nickel analogues like **2′b** under exceptionally mild conditions.[272, 273]



2′b **47′**

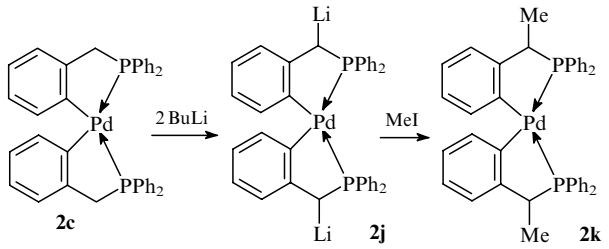
The structure of the products of formal insertion of alkyne into the M–C bond (complexes **47′**) was proved by various methods including X-ray diffraction analysis.[272, 273] Theoretical studies of insertion were carried out.[274]

If one takes into account the fact that the initial phosphanickelacycles are obtained by oxidative addition of *ortho*-bromo-substituted benzylphosphines to $[Ni(cod)_2]$, while their palladium analogues are prepared by direct intramolecular activation of the C–H bond in unsubstituted phosphine,[12, 54] development of similar processes for phosphapalladacycles seems quite a promising path in the regioselective organic synthesis.

2. Modification of phosphapalladacycles with retention of the Pd–C bond

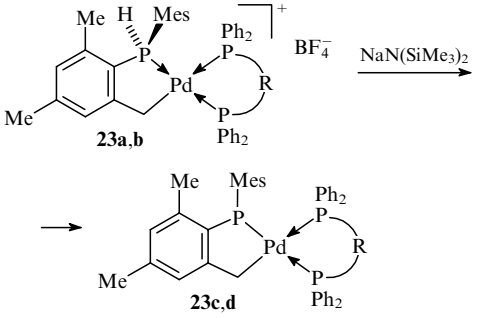
The functionalisation of P-donor ligands activated by cyclometallation not involving the Pd–C bond is even less studied. Of certain practical value is the electronic and steric modification of the benzylphosphine ligands incorporated in bis(chelate) cyclopalladated complexes by lithiation † into the α-position followed by 'quenching' of the carbanion formed with an appropriate electrophile.[71, 275]

† Note for comparison that reactions of CN-palladacycles with organolithium reagents involve the Pd–C bond.[264]



Using platinum analogues, it has been shown that this procedure ensures the introduction of not only alkyl groups but also silyl or phosphine groups (Me_3Si, Ph_2P) into the α-position of the benzyl fragment.[71,275] The reactions of cyclopalladated benzylphosphine ligands with salts of other metals, for example, with [AuCl(PPh$_3$)], give heterobimetallic compounds with two different M–C bonds.[275] An advantage of this method for modification of benzylphosphines is the regioselectivity of metallation, which involves only the α-benzyl position, whereas in the case of lithiation of free ligands, several routes are possible.[12]

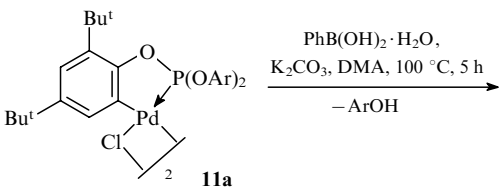
One more example of modification of a phosphapalladacycle not affecting the Pd–C and Pd–P bonds is the deprotonation of the cationic derivatives of the cyclopalladated secondary phosphine $HPMes_2$ (**23a** and **23b**) by treatment with the silylamides $M'N(SiMe_3)_2$ (M′ = Li or Na) as bases.[276]

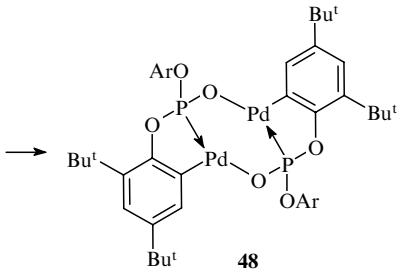


R = CH_2CH_2 (**23a**,**c**, 55%), *cis*-CH=CH (**23b**,**d**, 82%).

The resulting neutral complexes **23c**,**d**, containing an unusual non-charged phosphapalladacycle with a covalent Pd–P bond (rather than the coordination Pd ← P bond, as all of the structures considered previously), are distinguished by high stability and do not tend to decompose through the reductive elimination of the P–C bond. In the case of analogues of complexes **23c**,**d** with a monodentate phosphide (for example, [(dppe)MePd–P(H).Mes*]), this process takes place even below room temperature. It is typical of organometallic complexes with a terminal phosphide ligand.[276]

In order to evaluate the activation routes of phosphite- and phosphinite-based cyclopalladated catalysts, the behaviour of triarylphosphite derivative **11a** has been studied under the conditions used normally to prepare biaryls by the Suzuki reaction.[277] Heating of dimer **11a** with phenylboronic acid hydrate in dimethylacetamide (DMA) in the presence of a base furnished unusual CPC dimer **48**, containing the central six-membered $\{Pd_2P_2O_2\}$ ring (the structure of dimer **48** was established by X-ray diffraction).

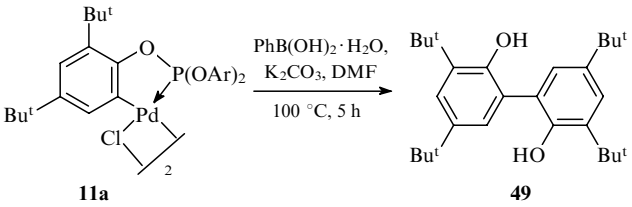




Ar = 2,4-$Bu^t_2C_6H_3$.

Dimer **48** is a cyclopalladated derivative of diarylphosphite $(ArO)_2P(OH)$ (H_2L^{48}), formed upon the hydrolytic elimination of an aryl group from the initial triarylphosphite HL[11]. The bridging function in dimer **48** is performed by the oxygen atoms of the deprotonated hydroxy group of the diarylphosphite ligand. The hydrated reagent $PhB(OH)_2 \cdot H_2O$ is assumed to serve as the source of water needed for hydrolysis.

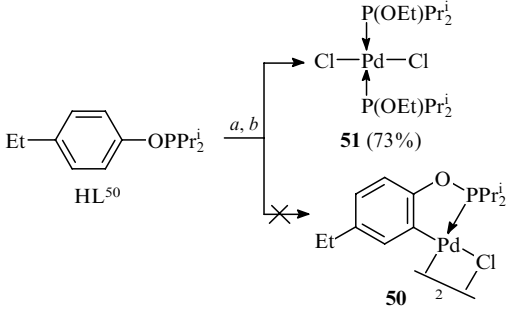
In the same reaction carried out in DMF, biphenol **49** was formed upon the oxidative coupling of two aryloxy fragments; its structure was confirmed by X-ray diffraction.[277]



Ar = 2,4-$Bu^t_2C_6H_3$.

The true mechanism of this transformation is unknown. The researchers consider two possible routes: (1) coupling involving free phenol molecules, liberated upon hydrolysis of CPC **11a** (see above), assisted by the metal centre; (2) coupling between two aryloxide fragments incorporated into phosphite ligands (this route includes intramolecular reorganisation and reductive elimination).

It is reasonable to suggest that the ligands in cyclopalladated phosphites and phosphinites can undergo not only hydrolysis but also solvolysis under appropriate conditions. Unfortunately, no reliable information on this subject is available; it is only known[277] that an attempted *ortho*-palladation of aryldialkylphosphinite HL[50] with $PdCl_2$ on refluxing in 2-methoxyethanol (MET) (*a*) followed by recrystallisation from a EtOH–CH_2Cl_2 mixture (*b*) gave, instead of the expected CPC **50**, coordination complex **51**, whose structure was proved by X-ray diffraction.



In the researchers' opinion, the new phosphinite $P(OEt)Pr^i_2$ (HL^{51}) is the product of transesterification of the initial ligand HL[50] with the solvent. However, the instant the solvolysis takes place remains unknown; this may occur either within the coordination intermediate $[Pd(HL^{50})_2Cl_2]$ or in the intermediate CPC **50**, because no attempts to carry out solvolysis of dimer **50** have been

made. It is only known[277] that palladium complexes with less electron-enriched aryl diarylphosphinites $P(OAr)Ar_2$ and triaryl phosphites $P(OAr)_3$ are not susceptible to transesterification.

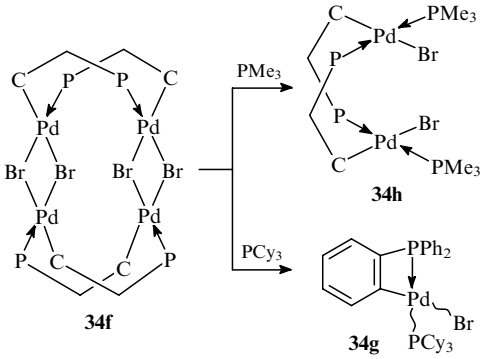
3. Dechelation and destruction of phosphapalladacycles

Three variants of cleavage of palladacycles without modification of the ligand structure are, in principle, possible: (1) transition to a monodentate coordination due to cleavage of the Pd ← E bond (E is the heteroatom); (2) the same due to cleavage of the Pd – C bond; (3) transformation of a chelating ligand into a bridging one. The first route is typical of CN-[111,198,278–280] and CO-palladacycles[281] with hard heterodonor nitrogen and oxygen atoms, which are readily displaced from the metal coordination sphere by excess auxiliary ligand with a softer donor atom (most often, phosphine). This gives mononuclear complexes *trans*-[(η^1-E⌒C)PdX(PR_3)$_2$] (E = N, O) with the monodentate η^1-C-bonded ligand (the heterodonor E atom remains in the non-coordinated state). The other two variants are unlikely for systems with hard heterodonor atoms, as they are weakly coordinated to soft palladium. To our knowledge, only one structure with a bridging CN-ligand has been reported.[282]

a. Dechelation of phosphapalladacycles

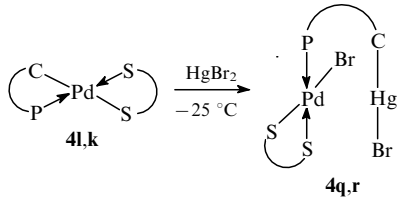
In the case of phosphapalladacycles, decoordination of the heterodonor atom appears problematic due to the strong binding of the soft phosphorus atom to the soft palladium centre. We have not found any examples of dechelation of PC-structures according to this pattern. The cleavage of PC-palladacycles is accompanied most often by transition of the ligand from the η^2-binding to bridging position.

As an illustration, one can consider the dechelation of cyclopalladated triphenylphosphine.[241] The steric strain of the four-membered phosphapalladacycle with the Pd – C(sp^2) bond accounts for its easy opening to give the tetramer [{Pd(μ-L^{34})(μ-X)}$_4$] (**34f**) with bridging P,C-bound ligands $(L^{34})^-$, which combine four metallic centres to form a macrocycle. The mononuclear species with this PC-palladacycle really exist in solutions only in the presence of excess auxiliary phosphine ligand, the equilibrium between complexes with ligands of two types — μ-L^{34} and η^2-L^{34} — being displaced towards the cyclopalladated structure (for example, **34g**) with an increase in the steric requirements of the auxiliary ligand (when $\theta > 150°$) .[241]



It is noteworthy that structures with the bridging PC-ligands like $(R_2PC_6H_4)^-$ are frequently encountered in dirhodium complexes,[283–288] in which they form the five-membered rings {RhPCCRh} involving the Rh_2 fragment.

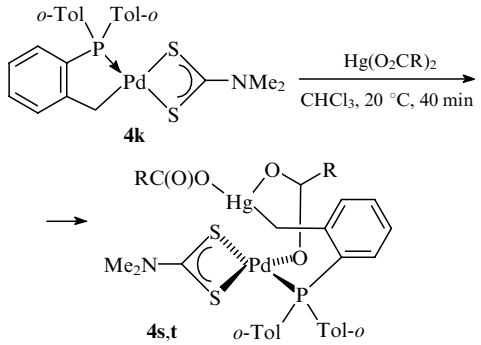
At first glance, this type of dechelation with transition from η^2- to μ-binding of the PC-ligand may seem impracticable for non-strained and rather stable five-membered phosphapalladacycles. Nevertheless, transformations of this type are still possible under certain conditions. For example, the reaction of xanthate (**4l**) and dithiocarbamate (**4k**) derivatives of cyclopalladated tris(*o*-tolyl)-phosphine with mercury bromide gave binuclear heterobimetallic compounds **4q**,**r** with the bridging anionic ligand (μ-L^4)$^-$ (see Ref. 53).



S⌒S — S_2COEt (**4l**,**q**), S_2CNMe_2 (**4k**,**r**);

P⌒C — 2-(*o*-Tol)$_2PC_6H_4CH_2$.

The dechelation giving analogous binuclear compounds **4s**,**t** has also been observed in the reaction of complex **4k** with mercury dicarboxylates.[122]



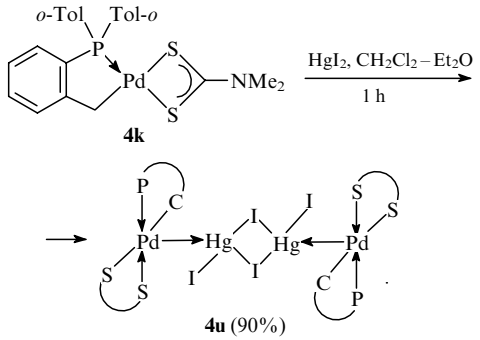
R = Me (**4s**, 79%), CF_3 (**4t**, 60%).

The structures of complexes **4q**[53] and **4s**[122] were proved by X-ray diffraction. In both cases, the bridging ligand $(L^4)^-$ remains P-coordinated to palladium, the carbanionic centre being lent to mercury. As was to be expected, compounds of this type are relatively unstable. For example, halide complexes **4q**,**r** dissociate in solutions at room temperature with recovery of the starting CPCs **4l**,**k**; this process can be 'frozen' by lowering the temperature to −55 °C only in the case of dithiocarbamate derivative **4k**.[53]

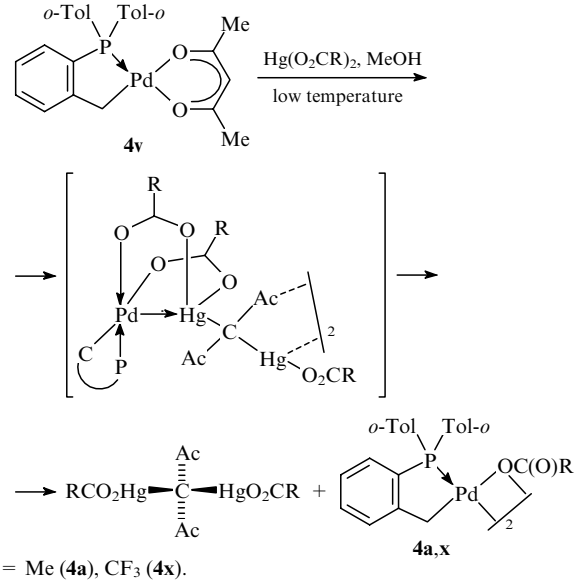
A number of unusual features of these processes deserve attention. First, fairly unexpected is the cleavage of the Pd – C covalent bond rather than the Pd←P coordination bond. In principle, this result can be attributed to stronger binding of palladium(II) to phosphorus than to the carbanionic fragment of the PC ligand (see Section II.2.c). However, the reason may also be in the reaction mechanism. The transmetallation is assumed[122] to occur *via* an electrophilic attack by the mercury salt on the Pd – C(sp^3) bond rather than on the Pd(II) centre or, the more so, the phosphorus atom.

The second unusual fact is that mercury(II), having high affinity to S-donor atoms, remains indifferent towards the dithiocarboxylate ligands. Note for comparison that an X-ray diffraction study of the structure of the binuclear compound [Pt(η^2-L^4)(κ^2:μ-S_2CNMe_2){Ag(PPh_3)}], isolated upon the reaction of the platinum analogue of complex **4k** with [Ag($OClO_3$)(PPh_3)], revealed the interaction of the silver ion with one sulfur atom of the dithiocabamate ligand.[123]

The third unusual fact is the strong influence of not only the nature of the metal incorporated into the PC-metallacycle but also the auxiliary ligand and the anion in the mercury salt on the reaction pathway. For example, in the reaction of dithiocarbamate **4k** with HgI_2 carried out under mild conditions, the PC-palladacycle is retained, the reaction yielding the tetranuclear complex with a dative Pd→Hg bond.[53]



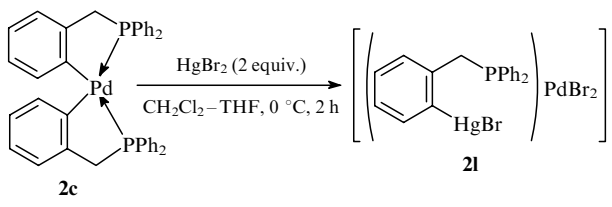
However, a close analogue of this complex — xanthate derivative **4l** of the same palladacycle — does not react with mercury iodide even on refluxing.[53] The reactions of the acetylacetonate derivative **4v** with mercury bromide and carboxylate were found to result in the recovery of the starting μ-bromide (**4w**) or μ-carboxylate dimeric CPCs (**4a** or **4x**). In the latter case, the β-diketonate ligand is displaced from the palladium(II) coordination sphere by mercury in the γ-C-bound state, as the compound $[Ac_2C(HgO_2CR)_2]$ (R = Me, CF_3).[121]



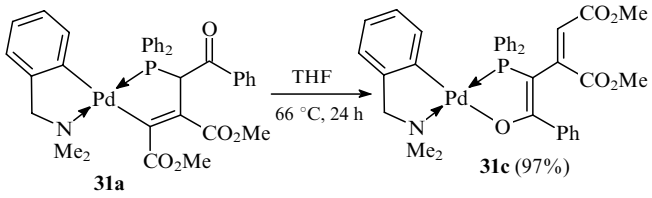
R = Me (**4a**), CF_3 (**4x**).

The behaviour of the platinum analogues in the reactions with mercury salts differs appreciably from the behaviour of PC-palladacycles such as **4**. For platinum systems, the formation of donor–acceptor Pt→Hg bonds is most typical;[53, 121, 289] the oxidative addition of HgX_2 to give Pt(IV) compounds is also possible.[122] However, no examples of dechelation of PC-platinacycles have been found so far.

Note that dechelation induced by mercuration has also been observed for a five-membered PC-palladacycle with a $C(sp^2)-Pd$ bond incorporated in *spiro*-complex **2c** when it has been made to react with mercury bromide.[71] In this case, mercury also attacks the carbon end of the palladacycle to give coordination complex **2l** with the monodentate P-coordinated *ortho*-mercurated phosphine.



An absolutely different principle underlies the cleavage of the phosphapalladacycle in *spiro*-complex **31a**. The thermolysis of this complex is accompanied by almost quantitative isomerisation of the PC-palladacycle into PO-chelating phosphinoenolate to give complex **31c**. This process also involves rupture of the Pd–C bond (but not the Pd←P bond) followed by 1,3-migration of hydrogen from the carbon atom adjacent to phosphorus to the metallated alkenyl carbon atom.[237, 239]

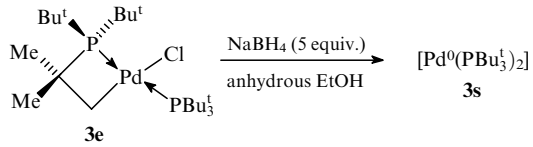


The structure of complex **31c** and the retention of the *E*-configuration of the exocyclic alkene fragment were confirmed by X-ray diffraction.[239] The researchers assume the tendency for the formation of a system of conjugated double bonds in the new β-phosphinoenolate ligand to be the driving force of the process.[237] However, if one estimates the relative stability of complexes **31a** and **31c** from the standpoint of the transphobia concept, the higher stability of the latter may be due to the replacement of the unfavourable *trans*-arrangement of two carbanionic centres (C–Pd–C) with the highest *trans*-effect in one axis by a more favourable combination of the softest and the hardest donor atoms on one diagonal (C–Pd–O). This also accounts for more preferred binding, unexpected at first glance, of the soft palladium to the hard enolate oxygen atom rather than to the soft carbanionic atom.

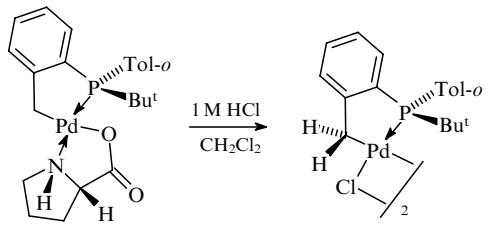
b. Destruction of phosphapalladacycles

A fundamentally different pattern of cleavage of phosphapalladacycles is induced by treatment with reducing agents or acids. In this case, the reaction involves the Pd–C bond and results in the recovery of the ligand HL. However, unlike these processes for CN-systems, in this case, the liberated ligand remains bound to palladium through the heteroatom to form a coordination compound. These reactions carried out with deuterated reagents (DCl or $LiAlD_4$) can be used, in principle, for regioselective introduction of an isotope label into the ligand molecule or to confirm cyclometallation and establish its path (for example, using mass spectrometry [290]).

The reduction of PC complexes can be used to prepare phosphine compounds of zerovalent palladium. For instance, treatment of dimer **3b** or its mononuclear adduct **3e** with the same phosphine HL^3 with sodium tetrahydroborate in ethanol results in the synthesis of the bis(phosphine) complex $[Pd^0(PBu^t_3)_2]$ (**3s**).[88, 102]



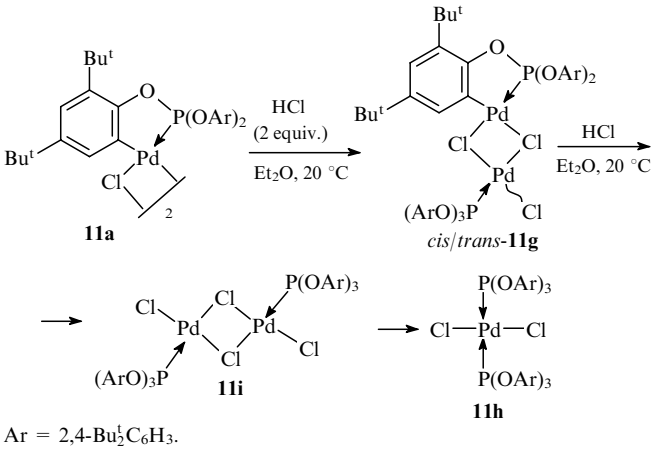
The classical PC-type complexes are not highly prone to protolysis. Treatment of mononuclear PC-palladacycles with a dilute aqueous solution of hydrochloric acid in a biphasic system with an organic solvent is often used to remove the auxiliary ligand (amine or amino acid) from these complexes (for example, in the optical resolution of the PC-palladacycles [79, 117, 125]). This procedure virtually does not affect the starting palladacycle, which can be recovered as the μ-chloride dimer (for example, **7a** [117]) in an almost quantitative yield.



(S_P,S_C,S_N)-**7g** (S_P)-**7a** (98%)

It is reasonable to suggest that the protolytic destruction of the PC-palladacycles can take place under more drastic conditions, for example, upon an increase in the strength and concentration of the acid and the reaction temperature and time and also on passing to homogeneous media. More evidence is provided by the fact that scalemic CN-palladacycle with the Pd–C* bond is fully racemised on long-term storage of its (*S*)-leucinate derivative in a solution of HCl in aqueous methanol.[291] When a weaker acid is used (AcOH in methanol), the enantiomeric composition changes insignificantly.[292]

Useful information on the course of acidolysis was gained from a spectroscopic (^{31}P NMR) study of the reactions of cyclopalladated phosphite **11a** with a stoichiometric amount of anhydrous hydrogen chloride in the organic medium.[69]



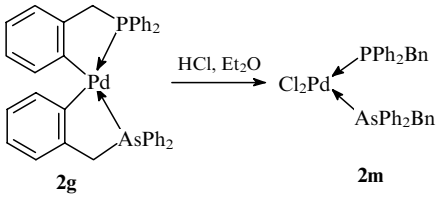
11a *cis*/*trans*-**11g** **11i** **11h**

Ar = 2,4-Bu$^t_2$C$_6$H$_3$.

The order in which the signals corresponding to the species shown in the scheme appear in the spectrum implies the initial destruction of only one of the two PC-palladacycles to give binuclear complex **11g** (as a ~4.8 : 1 mixture of *cis*- and *trans*-isomers). The subsequent cleavage of the second palladacycle yields binuclear coordination complex **11i** with monodentate ligands HL[11], which is partially converted into mononuclear analogue **11h**. Three hours later, the ratio of the initial complex to the complexes formed upon protolysis, **11a** : **11g** : **11i** : **11h**, was 8.5 : 37.5 : 52 : 2, indicating rather high stability of the PC-palladacycles of this type against protolysis: almost a half of the phosphite ligand retains the cyclopallated structure.

The susceptibility of phosphapalladacycles to protolysis markedly increases when they are incorporated into *spiro*-structures. The reactions of these complexes with hydrogen chloride are exothermal; they are carried out at reduced temperatures.[71] The reactions give mono- or binuclear coordination compounds of palladium(II) with *ortho*-unsubstituted benzylphosphines.[71–73] The geometry of the mononuclear products like [Pd(HL)$_2$Cl$_2$] depends on the steric situation at the P-donor atom: the coordination compounds of sterically less hindered phosphines PhCH$_2$PR$_2$ (R = Me, Ph) are formed as mixtures of *cis*- and *trans*-isomers, whereas for more bulky di(*tert*-butyl)benzylphosphine, this process is selective and gives only the *cis*-isomer.[71]

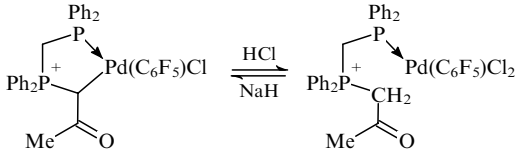
The practical use of these transformations appears problematic in view of the multistage character of the synthesis of *spiro*-PC-complexes *via ortho*-bromo-substituted benzylphosphines.[12] These reactions may be of some practical value as applied to heteroligand *spiro*-structures, which are converted upon protolysis into mixed-ligand coordination compounds. For example, the reaction of complex **2g** with a stoichiometric amount of hydrogen chloride gave arsino-phosphine coordination complex **2m** in a high yield.[72, 73]



2g **2m**

It should be noted that the protolytic stability of phosphapalladacycles in *spiro*-structures is higher than the stability of their N- and As-analogues. Spectroscopic studies of the behaviour of mixed-ligand *spiro*-complexes **2g** and *cis*-[(η^2-L^2)Pd(η^2-C$_6$H$_4$CH$_2$NMe$_2$)] (**2e**) in relatively weak acetic acid have shown that in both cases, protolysis takes place for the less stable AsC- or CN-metallacycle, whereas the PC-palladacycle is retained as dimeric CPC **2b** with acetate bridges.[293] Note that in a stronger acid (HCl), both palladacycles of complex **2g** are destroyed, benzylamine is removed as the ammonium salt, while benzylphosphine HL^2 remains in the metal coordination sphere in the resulting binuclear complex [{Pd(κ^1-HL^2)Cl(μ-Cl)}$_2$].[72]

The phosphino-P-ylide palladacycles are also destroyed under the action of acids to give coordination complexes with the monodentate P-bonded cationic phosphonio-phosphine.[133] However, unlike the reactions of *spiro*-complexes considered above, the protonation of phosphino-P-ylide CPC is reversible, and the phosphapalladacycle can be regenerated by deprotonation of phosphonium ligands in coordination species. Thus complex **16g**, formed upon the protolysis of complex **16h**, can be recovered in the initial state on treatment with sodium hydride in THF.[133]



16h *cis*/*trans*-**16g** (70%)

The information presented in this Section demonstrates that the data on the reactivity of phosphapalladacycles are scarce, which calls for further systematic research along this line.

IV. Conclusion

The future development of the chemistry of phosphapalladacycles is of interest not only from the fundamental standpoint; its topicality is determined first of all by the demands of homogeneous catalysis, which has entered a new phase after PC- and PCP-complexes have been included in the range of available (pre)catalysts. Several promising lines of research can be distinguished.

First, one should expect the solution of the mechanistic problem related to the true role of phosphapalladacycles in the catalysis: whether they function as such in the catalytic cycle or serve only as convenient sources of zerovalent palladium? This point is still debated. With rare exceptions,[294] the possibility of the Pd^{II}/Pd^{IV} interconversion in a catalytic cycle[2, 3, 6, 295] is considered together with classical Pd^{II}/Pd^0 schemes;[2, 5, 294] it has also been suggested that a PC-palladacycle can be retained as an anionic Pd^0-containing intermediate.[296] Elucidation of the behaviour of phosphapalladacycles in catalytic processes requires conducting the reactions under stoichiometric conditions with isolation or spectroscopic identification of possible intermediates. Therefore, knowledge of the reactivity of phosphapalladacycles becomes especially important.

Realisation of the fact that the efficiency of many classical catalytic systems containing palladium(0) and bulky monodentate phosphines may be determined by the *in situ* generation of PC-species can also stimulate further, more extensive development of the chemistry of phosphapalladacycles. Indeed, the unique efficiency of these catalytic systems in the cross-coupling and the formation of carbon–heteroatom bonds is known. It is also evident that under conditions standard for the reactions of this type (80–160 °C, the presence of a base), the formation of PC-palladacycles with ligands such as PBu^t_3,[297–299] P(Tol-*o*)$_3$,[297, 300, 301] P(OAr)$_3$ [302] and 2-phosphinobiaryls [303, 304] is inevitable.

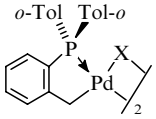
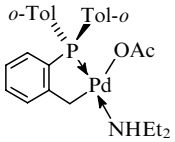
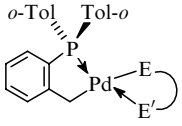
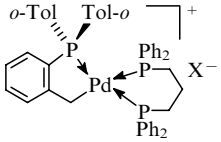
Even if the role of PC- or PCP-complexes in some reactions would be restricted only to the supply of palladium(0) into the catalytic cycle, the unique thermal and hydrolytic stability of these compounds makes them fairly promising as (pre)catalysts. Many phosphapalladacycles withstand long-term heating (up to 300 h, 140–320 °C) without any signs of decomposition,[295, 305–307] which allows one to avoid the precipitation of palladium black during the process.[302] Therefore, more extensive involvement of not only standard (usually dimeric) PC-palladacycles but also their various derivatives into catalytic processes should be expected. The results obtained to date [14–19, 22] demonstrate that modification of the environment of the metallic centre in these complexes can serve as a potent method for increasing their catalytic activity.

This calls for systematic research into the *trans*-effect behaviour in cyclopalladated compounds. It is necessary to compose detailed STE and KTE sequences for C- and P-donor atoms of various types incorporated in phosphapalladacycles, confirmed by several methods (X-ray diffraction, NMR and IR). The knowledge of these regularities is important not only for structural studies of compounds of this type but also for their practical use. Indeed, the catalytic activity is known to be often correlated with the ligand STE.[139, 168]

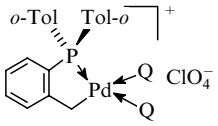
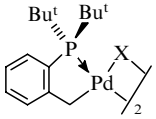
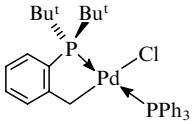
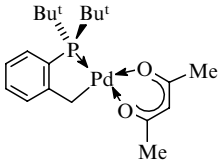
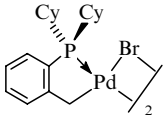
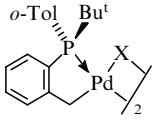
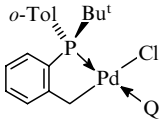
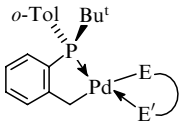
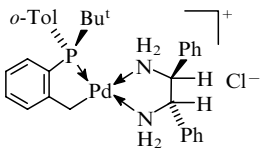
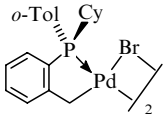
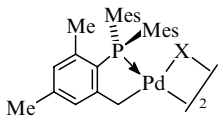
An important place (as regards the prospects for further development of the chemistry of phosphapalladacyclic structures) should belong to the development of diverse versions of regioselective organic synthesis based on the reactivity of the Pd–C bonds, first, in the stoichiometric version and, perhaps in the future, in the catalytic version. The functionalisation of P-donor ligands through cyclopalladated intermediates should hold the priority in this field. This strategy opens the way to new types of bidentate ligands (diphosphine, aminophosphine, *etc*.) useful for catalysis, in particular, for enantioselective catalysis. Its compatibility with the traditional routes involving *ortho*-lithiated intermediates is obvious: cyclopalladation is usually markedly facilitated in sterically overcrowded systems,[12, 308] whereas the lithiation directed by the donor atom is, conversely, hampered or even becomes impossible.[309]

V. Supplements

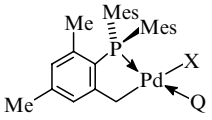
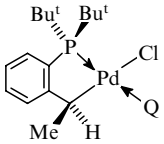
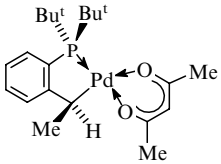
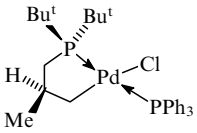
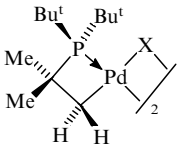
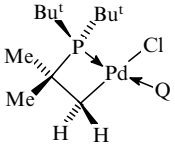
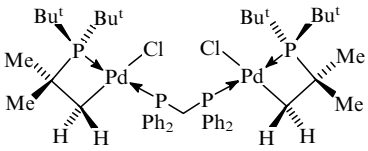
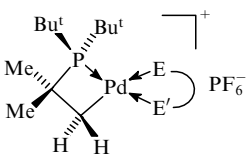
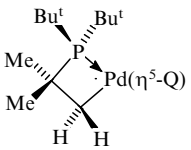
Supplement 1. Derivatives of classical phosphapalladacycles of the PC type.

Complex	Number of the compound [a]	Q or E⌒E′	X	$^2J_{PP}$ /Hz	Starting complexes, reagents and reaction conditions [b]	Yield (%) [c]	Ref.
Five-membered palladacycles with the C(sp^3)–Pd bond							
	**4b**		pz$^-$		**4a**, pzH, NEt_3, MeOH, Δ, 1 h	91	64
	4c		4-mpz$^-$		**4a**, 4-mpzH, NEt_3, MeOH, Δ, 1 h	87	64
	4d		3,5-dmpz$^-$		**4a**, 3,5-dmpzH, NEt_3, MeOH, Δ, 1 h	97	63, 64
	4g		Cl		1) **4a**, LiCl, MeOH–CH_2Cl_2, 20 °C	99.7	53
					2) **4a**, $[Bu_4N]Cl$, CH_2Cl_2, 20 °C, 1 h	100	51
	4w		Br		**4a**, $[Bu_4N]Br$, CH_2Cl_2, 20 °C, 1h	98	51
	**4y** *				**4a**, $HNEt_2$, C_5H_{12}, 70 °C, 30 min	84	294
	**4k**	$Me_2NC(S)S^-$			*a*) **4g**, $AgClO_4$, THF, 20 °C, 15 min; *b*) $NaS_2CNMe_2 \cdot 2H_2O$, MeOH	94	53
	4l	$EtOC(S)S^-$			*a*) **4g**, $AgClO_4$, THF, 20 °C; *b*) KS_2COEt, THF, 20 °C, 15 min	76	53
	4m	$pz_2BH_2^-$			**4w**, $K[pz_2BH_2]$, Me_2CO, 20 °C, 24 h	96	116
	4n*	pz_3BH^-			**4w**, $K[pz_3BH]$, Me_2CO, 20 °C, 24 h	100	116
	4p*	2-$AcC_6H_4O^-$			**4a**, 2-AcC_6H_4OH, PhMe, $KOBu^t$, 20 °C, 12 h	86	118
	4v	$acac^-$			**4g**, Tl(acac) (2 equiv.), $CHCl_3$, Δ	–	121
	4z	2-Ac-4-$FC_6H_3O^-$			**4a**, 2-Ac-4-FC_6H_3OH, PhMe, $KOBu^t$, 20 °C, 12 h	92	118
	4aa*	2-$BzC_6H_4O^-$			**4a**, 2-BzC_6H_4OH, PhMe, $KOBu^t$, 20 °C, 12 h	77	118
	4bb*	2-$AcC_{10}H_6O^-$			**4a**, 2-$AcC_{10}H_6OH$, PhMe, $KOBu^t$, 20 °C, 12 h	79	118
	4cc	2-Bz-4-$MeC_6H_3O^-$			**4a**, 2-Bz-4-MeC_6H_3OH, PhMe, $KOBu^t$, 20 °C, 12 h	76	118
	**4i**		Cl		**4g**, $Ph_2P(CH_2)_3PPh_2$, MeOH, 20 °C, 3 h	–	30
	4j		PF_6	333 (*trans*), 36 (*cis*)	*a*) **4g**, $Ph_2P(CH_2)_3PPh_2$, MeOH, 20 °C, 3 h; *b*) $[NH_4]PF_6$, MeOH–H_2O	85	30

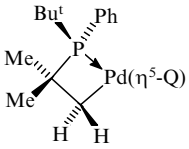
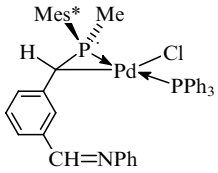
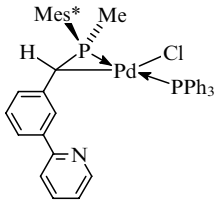
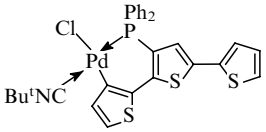
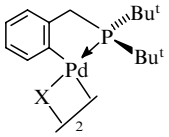
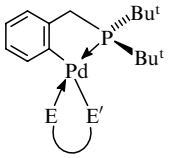
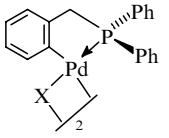
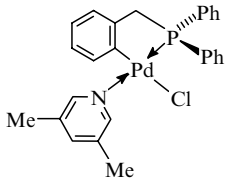
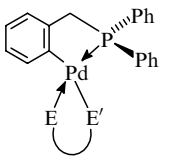
Supplement 1 (continued).

Complex	Number of the compound [a]	Q or E⌒E′	X	$^2J_{PP}$ /Hz	Starting complexes, reagents and reaction conditions [b]	Yield (%) [c]	Ref.
Five-membered palladacycles with the C(sp^3) – Pd bond							
	**4f**	$Ph_3P=NCN$			*a*) **4g**, $AgClO_4$, MeCN, 20 °C; *b*) $Ph_3P=NCN$, CH_2Cl_2, 20 °C, 30 min	55	105
	4h	MeCN			**4g**, $AgClO_4$, MeCN, 20 °C [d]	–	105
	**8c**		OAc		**8a**, AgOAc, Me_2CO, 20 °C, 12 h	80	60
	8d		OBz		**8a**, AgOBz, Me_2CO, 20 °C, 12 h	71	60
	**8b**			382	**8a**, PPh_3 (2.5 equiv.), CH_2Cl_2	95	60
	**8c**				**8a**, Tl(acac), PhH, 20 °C, 5 h	63	60
	**52**				[{Pd(η^2-L^{52})(μ-OAc)}$_2$], $[Bu_4N]Br$, CH_2Cl_2, 20 °C, 1 h	53	51
	**7d**		OAc		**7a**, AgOAc, Me_2CO, 20 °C, 12 h	77	60
	7h		OBz		**7a**, AgOBz, Me_2CO, 20 °C, 12 h	65	60
	**7b**	(–)-α-MBA			**7a**, (–)-α-MBA, CH_2Cl_2, 20 °C, 1h	91	60
	7e [e]	d_5-Py			**7a**, d_5-Py, $CDCl_3$, 20 °C, 5 min	(~100) [f]	90
	7f	PPh_3		401	1) **7a**, PPh_3 (2.1 equiv.), PhH, 50 °C, 1 min	84	60
	7f [e]	PPh_3		399 (*trans*), 42 (*cis*)	2) **7a**, PPh_3, PhH, 50 °C, 10 min	84	117
	7i [e]	Py			**7a**, Py, CH_2Cl_2, 20 °C, 5 min	79	60
	**7g** [g]	(*S*)-Pro$^-$			1) **7a**, (*S*)-ProK, $CH_2Cl_2-H_2O$, 20 °C, 1h	76	117
	7g [g]	(*S*)-Pro$^-$			2) **7a**, (*S*)-ProK, MeOH, 20 °C, 1h	~100	117
	7j	acac$^-$			**7a**, Tl(acac), CH_2Cl_2, 20 °C, 30 min	70	60
	**7c**				**7a**, (*R,R*)-stien, CH_2Cl_2, 20 °C, 1h	92	60
	**53**				[{Pd(η^2-L^{53})(μ-OAc)}$_2$], $[Bu_4N]Br$, CH_2Cl_2, 20 °C, 1 h	–	51
	**1b**		Br		1) **1a**, $[Bu_4N]Br$, CH_2Cl_2, 20 °C, 1 h	86	51
					2) **1c**, KBr, Me_2CO, 20 °C	44	55
	1c		Cl		**1a**, $[Bu_4N]Cl$, CH_2Cl_2, 20 °C, 1 h	–	51
	1e		I		**1c**, KI or NaI, Me_2CO, 20 °C	83	55
	1f		pz$^-$		**1c**, pzH, NaOH – MeOH, 20 °C, 20 h	80	62

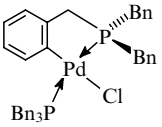
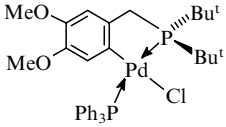
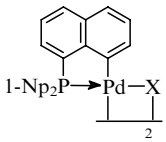
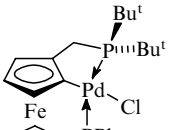
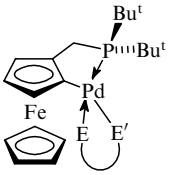
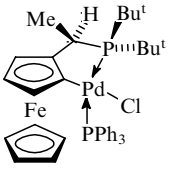
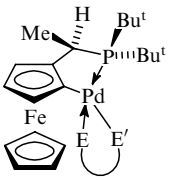
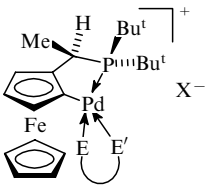
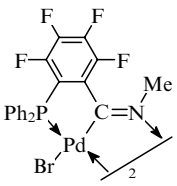
Supplement 1 (continued).

Complex	Number of the compound [a]	Q or E⌒E′	X	$^2J_{PP}$ /Hz	Starting complexes, reagents and reaction conditions [b]	Yield (%) [c]	Ref.
Five-membered palladacycles with the C(sp^3)–Pd bond							
	**1d**	4-$Me_2NC_5H_4N$	Cl		**1c**, 4-$Me_2NC_5H_4N$ (excess), $CDCl_3$, 20 °C	–	92
	1g	PPh_3	Cl	419	**1c**, PPh_3, PhH, Δ, 30 min, N_2	97	94
	1h	PPh_3	Br	416	see [h]	–	94
	1i	PPh_3	I	414	see [h]	–	94
	1j	PPh_3	pz^-	420	see [h]	–	94
	1k	$AsPh_3$	Cl		**1c**, $AsPh_3$, PhH, Δ, 1.5 h, N_2	85	94
	1l	DBP	Cl	421	**1c**, DBP, PhH, Δ, 30 min, N_2	85	94
	1m	$P(OPh)_3$	Cl	607	**1c**, $P(OPh)_3$, PhH, Δ		94
	**54a**	PPh_3			[{Pd(η^2-L^{54})(μ-OAc)}$_2$], PPh_3 (2.2 equiv.), PhH, Δ	82	97
	54b	PMe_2Ph			[{Pd(η^2-L^{54})(μ-OAc)}$_2$], PMe_2Ph (2.2 equiv.), PhH, Δ	76	97
	**54c**				[{Pd(η^2-L^{54})(μ-OAc)}$_2$], Tl(acac), PhH, 20 °C, 22 h	58	97
	**55**			371	[{Pd(η^2-L^{55})(μ-Cl)}$_2$], PPh_3, PhH, Δ, 5 min	–	99
Four-membered palladacycles with the C(sp^3)–Pd bond							
	**3a**		Cl, MeO		**3b**, MeOH, NaOH, 40 °C, 2 h	70	61
	**3c**	PPh_3		422	**3b**, PPh_3, PhH, 20 °C, 12 h	–	88
	3d [i]	$AsPh_3$			**3b**, $AsPh_3$, PhH, 20 °C, 12 h	–	88
	3f	diars			**3b**, diars, PhH, 20 °C, 12 h, N_2	68	106
	3g	bipy			**3b**, bipy, PhH, 40 °C, 8 h	74	106
	3h	ape		420	**3b**, ape, PhH, 40 °C, 5 h	86	106
	3p	Py			**3b**, Py, PhH, 20 °C, 2 h	–	88
	3t	PCy_3		409	**3b**, PCy_3, PhH, 20 °C, 12 h	–	88
	3u	PEt_3		441	**3b**, PEt_3, PhH, 20 °C, 12 h	–	88
	3v	PPr^i_3		403	**3b**, PPr^i_3, PhH, 20 °C, 12 h	–	88
	3w	PPh_2Me		440	**3b**, PPh_2Me, PhH, 20 °C, 12 h	–	88
	3x	PBu^t_2Me		413	**3b**, PBu^t_2Me, PhH, 20 °C, 12 h	–	88
	3y	P(*o*-Tol)$_3$		413	**3b**, P(*o*-Tol)$_3$, PhH, 20 °C, 12 h	–	88
	**3j**			420	**3b**, dppm (2 equiv.), PhH, 20 °C, 6 h	89	106
	**3k**	ape		360	*a*) **3b**, $AgPF_6$, CH_2Cl_2–Me_2CO, 20 °C, 30 min; *b*) ape, CH_2Cl_2, 20 °C, 4 h	78	106
	3l	diars			*a*) **3b**, $AgPF_6$, CH_2Cl_2–Me_2CO, 20 °C, 30 min; *b*) diars, 20 °C, 5 h	74	106
	3m	bipy			*a*) **3b**, $AgPF_6$, CH_2Cl_2–Me_2CO, 20 °C, 30 min; *b*) bipy, 20 °C, 5 h	69	106
	**3n**	Cp			**3b**, TlCp, PhH, 20 °C, 30 min	77	124
	3z	Cp*			**3b**, LiCp*, PhH, 20 °C, 3 h	60	124

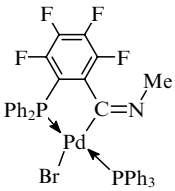
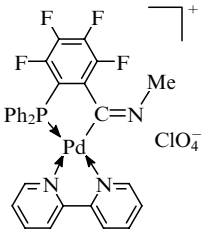
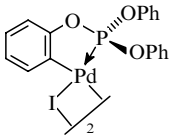
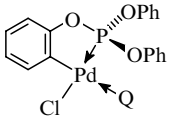
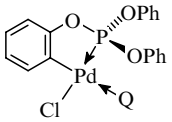
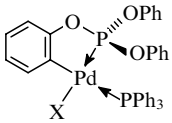
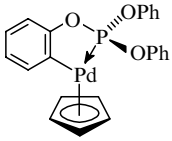
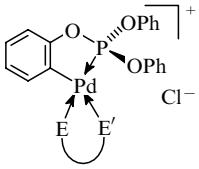
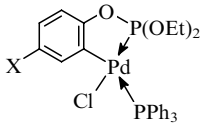
Supplement 1 (continued).

Complex	Number of the compound [a]	Q or E⌒E′	X	$^2J_{PP}$ /Hz	Starting complexes, reagents and reaction conditions [b]	Yield (%) [c]	Ref.
Four-membered palladacycles with the C(sp^3)—Pd bond							
	**13b**	Cp			**13a**, TlCp, PhH, 20 °C, 30 min	67	124
	13c	Cp*			**13a**, LiCp*, PhH, 20 °C, 3 h	39	124
Three-membered palladacycles with the C(sp^3)—Pd bond							
	**56**			397	[{Pd(η^2-L^{56})(μ-OAc)}$_2$], PPh_3, CH_2Cl_2, 20 °C, 10 min	80	96
	**57**			393	[{Pd(η^2-L^{57})(μ-OAc)}$_2$], PPh_3, CH_2Cl_2, 20 °C, 10 min	67	96
Six-membered palladacycles with the C(sp^2)—Pd bond							
	**18**				[Pd(η^2-L^{18})(μ-Cl)$_2$], Bu^{t}NC, CH_2Cl_2, N_2, 25 °C, 0.5 h	78	173
Five-membered palladacycles with the C(sp^2)—Pd bond							
	**5a**		Cl		[Pd(η^2-L^5)$_2$], [$PdCl_2(SEt_2)_2$], $CHCl_3$, Δ, 1–2 h	100	67
	5f		Br		1) [Pd(η^2-L^5)$_2$], $HgBr_2$, THF, 20 °C, 1 h; Δ, 5 h	92	67
					2) **5a**, LiBr, Me_2CO, 20 °C, 20 h	80	57
	5g		I		**5a**, NaI, Me_2CO, 20 °C, 20 h	85	57
	**5c**	2-$Me_2PCH_2C_6H_4$		22	**5a**, 2-$Me_2PCH_2C_6H_4Li$, Et_2O, −20 to 20 °C, 2 h	61	71
	5e	2-$Ph_2PCH_2C_6H_4$		19	**5a**, 2-$Ph_2PCH_2C_6H_4Li$, PhH, 20 °C, ~2 h	87	71, 232
	5h	acac			**5a**, Tl(acac), PhH, 20 °C, 2.5 h	94	57
	**2a**		Cl		1) [Pd(η^2-L^2)$_2$], $PdCl_2$, $Me_2C_6H_4$, Δ	–	67
					2) [Pd(η^2-L^2)$_2$], [$PdCl_2(SEt_2)_2$], $CHCl_3$, Δ, 1–2 h	92	67
					3) **2b**, LiCl, Me_2CO-H_2O, 20 °C, 24 h	86	54
	2b		OAc		**2a**, AgOAc, Me_2CO, 20 °C, 24 h	76	54
					1) [Pd(η^2-L^2)$_2$], $Hg(OAc)_2$, THF, 20 °C, 1 h; Δ, 5 h	77	67
	2d		Br		2) [Pd(η^2-L^2)$_2$], $HgBr_2$, THF, 20 °C, 1 h; Δ, 5 h	86	67
	**2i**				**2b**, 3,5-dmpy, Me_2CO, 20 °C, 20 h	50	54
	**2f**	$acac^-$			**2a**, Tl(acac), CH_2Cl_2, 20 °C, 20 h	41	54
	2g	2-$Me_2NCH_2C_6H_4$			**2a**, 2-$Me_2NCH_2C_6H_4Li$, Et_2O, −20 to 20 °C, 2–3 h	89	72, 73
	2h	2-$Me_2AsCH_2C_6H_4$			**2a**, 2-$Me_2AsCH_2C_6H_4Li$, Et_2O, −20 to 20 °C, 2–3 h	46	72, 73
	2n	2-$Ph_2AsCH_2C_6H_4$			**2a**, 2-$Ph_2AsCH_2C_6H_4Li$, Et_2O, −20 to 20 °C, 2–3 h	82	72, 73

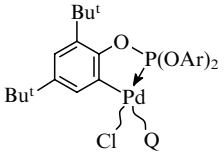
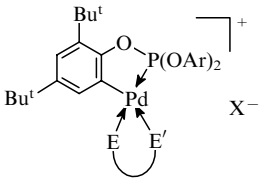
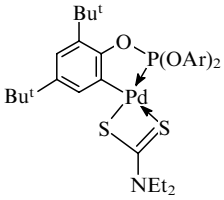
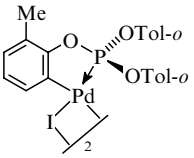
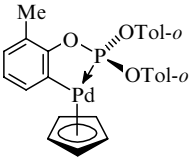
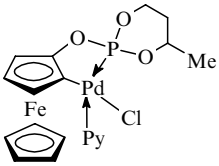
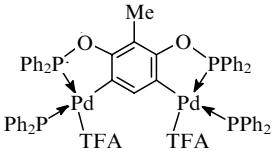
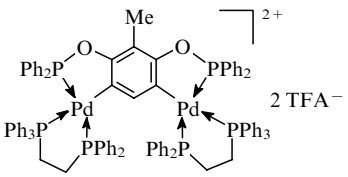
Supplement 1 (continued).

Complex	Number of the compound [a]	Q or E⌒E′	X	$^2J_{PP}$ /Hz	Starting complexes, reagents and reaction conditions [b]	Yield (%) [c]	Ref.
Five-membered palladacycles with the C(sp^2) – Pd bond							
	**29**				$[Pd(\eta^2\text{-}L^{29})(\mu\text{-}Cl)]_2$, PBn_3	–	311
	**58**			395	$[\{Pd(\eta^2\text{-}L^{58})(\mu\text{-}Cl)\}_2]$, PPh_3 (2.2 equiv.), EtOH, Δ, 10 min	67	98
	**59a**		I		–	–	22
	59b		Br		–	–	22
	**9b**			398	**9a**, PPh_3 (2.1 equiv.), PhH, 20 °C, 20 min	91	79
	**9c** [j]	(*S*)-Pro$^-$			**9a**, (*S*)-ProK, MeOH, 20 °C, 3 h	96	79
	**10b***			399	**10a**, PPh_3 (2.1 equiv.), PhH, 20 °C, 20 min	79	78
	**10c**	acac$^-$			**10a**, acacH, KOH, MeOH, 20 °C, 5.5 h	28	90
	10d [j]	(*S*)-Pro$^-$			**10a**, (*S*)-ProK, MeOH, 20 °C, 2 h	94	90
	**10e**	phen	PF_6		*a*) **10a**, phen, MeOH, 20 °C, 4 h; *b*) KPF_6, H_2O, 20 °C, 30 min	70	90
	10f [j]	(*R,R*)-stien	Cl		**10a**, (*R,R*)-stien, MeOH, 20 °C, 1 h	(~100)	90
	**60a**				$[\{PdCl(\eta^3\text{:}\mu\text{-}L^{60})\}_2]$, KBr, Me_2CO	–	56

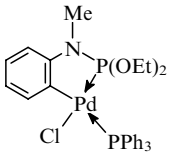
Supplement 1 (continued).

Complex	Number of the compound [a]	Q or E⌒E′	X	$^2J_{PP}$ /Hz	Starting complexes, reagents and reaction conditions [b]	Yield (%) [c]	Ref.
Five-membered palladacycles with the C(sp^2) – Pd bond							
	**60b**				[{PdCl(η^3:μ-L^{60})}$_2$], PPh_3, Me_2CO, 20 °C	–	56
	**60c**				[{PdCl(η^3:μ-L^{60})}$_2$], bipy, $NaClO_4$, Me_2CO, 20 °C	–	56
	**14f**				**14b**, NaI, Me_2CO, 20 °C	95	58
	**14c**	PPh_3		48	**14b**, PPh_3, CH_2Cl_2, 20 °C, 10 min	96	58
	14d	$P(OMe)_3$		55	**14b**, $P(OMe)_3$, CH_2Cl_2, 20 °C, 10 min	89	58
	14g	$P(OPh)_3$		56	**14b**, $P(OPh)_3$, CH_2Cl_2, 20 °C, 10 min	99	58, 242
	14h	$AsPh_3$			**14b**, $AsPh_3$	–	58
	**14i**	Py			**14b**, Py, CH_2Cl_2, 20 °C	94	58
	14j	Bu^{t}NC			**14b**, Bu^{t}NC (2 equiv.)	100	58
	14k	CyNC			**14b**, CyNC (2 equiv.)	100	58
	**14e**		Me	32	*a*) **14b**, PPh_3, MeLi, PhH, 5 °C, 1 h; *b*) MeOH	70	74
	14l		Ph	35	*a*) **14b**, PPh_3, PhLi, PhH, 5 °C, 1 h; *b*) H_2O	–	74
	14m		n-$C_5H_{11}C\equiv C$	35	*a*) **14b**, PPh_3, n-$C_5H_{11}C\equiv CLi$, PhH, 5 °C, 1 h; *b*) H_2O	–	74
	**14a** *				**14b**, TlCp, THF, 20 °C, 16 h	72	58
	**14n**	dppe		515 (*trans*), 30 (*cis*)	**14b**, dppe, $CDCl_3$	100	58
	**61a**		MeO	45	–	90	58
	61b		Me	47	–	90	58
	61c		NO_2	42	–	90	58

Supplement 1 (continued).

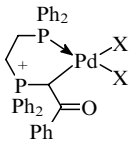
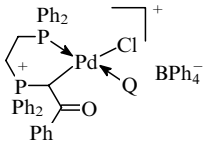
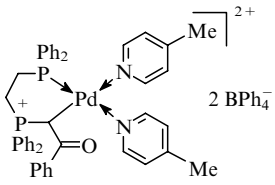
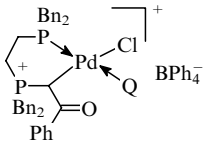
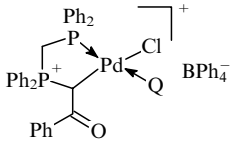
Complex	Number of the compound [a]	Q or E⌒E′	X	$^2J_{PP}$ /Hz	Starting complexes, reagents and reaction conditions [b]	Yield (%) [c]	Ref.
Five-membered palladacycles with the C(sp²) – Pd bond							
 (Ar = 2,4-$Bu^t_2C_6H_3$)	**11b**	$P(OMe)_3$		53	**11a**, $P(OMe)_3$, CH_2Cl_2, 20 °C, 30 min	62	69
	11f	PPh_3		604 (*trans*), 41 (*cis*)	**11a**, PPh_3, CH_2Cl_2, 20 °C, 30 min	92 [f]	69
	11j	$P(OEt)_3$		50	**11a**, $P(OEt)_3$, CH_2Cl_2, 20 °C, 30 min	41	69
	11k	$P(OPh)_3$		52	**11a**, $P(OPh)_3$, CH_2Cl_2, 20 °C, 30 min	41	69
	11l	PCy_3		41	**11a**, $Cy_3P \cdot CS_2$, PhMe, 110 °C, 2 h	61	69
 (Ar = 2,4-$Bu^t_2C_6H_3$)	**11d**	dppf	OTf	540 (*trans*), 52 (*cis*)	*a*) **11a**, AgOTf, MeCN, 20 °C, 5 min; *b*) dppf, 20 °C, 1 h	65	69
	11m	dppe	Cl	502 (*trans*), 33 (cis)	**11a**, dppe, CH_2Cl_2, 20 °C, 30 min	96	69
 (Ar = 2,4-$Bu^t_2C_6H_3$)	**11e***				**11a**, $[Et_2NCS_2]Na \cdot 3H_2O$, CH_2Cl_2 – EtOH – H_2O (10 : 10 : 1), 20 °C, 5 min	63	69
	**62a**			see [k]	[{Pd(η²-L^{62})(μ-Cl)}₂], NaI, Me_2CO, 20 °C	95	59
	**62b**				[{Pd(η²-L^{62})(μ-Cl)}₂], TlCp, THF, 20 °C, 15 h	70	59
	**63*** (see [l])				[{Pd(η²-L^{63})(μ-Cl)}₂], Py, CH_2Cl_2	–	89
	**12b**			28	[{Pd_2(η²:η²-L^{12})(μ-TFA)}₂]*, PPh_3, CH_2Cl_2, 20 °C, 18 h	–	115
	**12c** [m]			379 (*trans*), 24 (*cis*)	[{Pd_2(η²:η²-L^{12})(μ-TFA)₂}₂],* dppe, CH_2Cl_2, 20 °C, 18 h	–	115

Supplement 1 (continued).

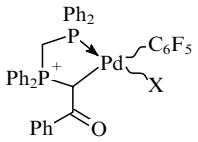
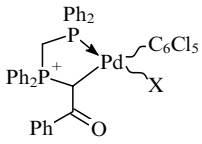
Complex	Number of the compound [a]	Q or E⌒E′	X	$^2J_{PP}$ /Hz	Starting complexes, reagents and reaction conditions [b]	Yield (%) [c]	Ref.
Five-membered palladacycles with the C(sp^2) – Pd bond							
	**64**			46	–	–	58

[a] The complexes studied by X-ray diffraction are asterisked. [b] Here and below, the digits designate different methods for the preparation of a complex, while letters mark the preparation stages. [c] The isolated yield is given; the yield determined from spectroscopic data is indicated in parentheses. [d] The synthesis was carried out under conditions described [310] for the Pt-analogue. [e] The complex exists in solution as a mixture of *cis*- and *trans*-isomers. [f] The complex was generated *in situ* and identified by spectroscopy. [g] The complex represents a mixture of two diastereomers (1 : 1), each existing as geometric *cis*- and *trans*-isomers (^{31}P NMR). [h] The complex was prepared similarly to the chloride analogue. [i] The adduct is unstable and dissociates in solutions. [j] The complex consists of two diastereomers. [k] For the adduct with P(Tol-*o*)$_3$, the constant $^2J_{PP}$ = 54 Hz is given.[242] [l] A mixture of two diastereomeric racemates. [m] Mixed with a small amount of tetranuclear species with a bridged phosphine.

Supplement 2. Derivatives of phosphino-P-ylide PC-palladacycles.

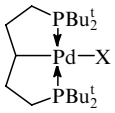
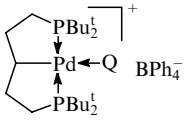
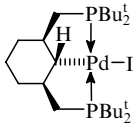
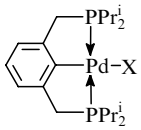
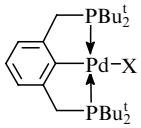
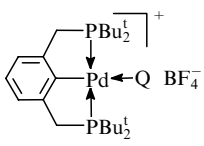
Complex	Number of the compound	Q	X	Starting complexes,[a] reagents and reaction conditions	Yield (%) [c]	Ref.
Six-membered palladacycles						
	**15b** [b]		NCS	**15a**, KSCN, MeOH – CH_2Cl_2	26	130, 131
	15k		Br	**15a**, NaBr, MeOH – CH_2Cl_2	59	130, 131
	15l		I	**15a**, NaI, MeOH – CH_2Cl_2	24	130, 131
	**15d**	PPh_3		**15a**, PPh_3, $NaBPh_4$, CH_2Cl_2, 20 °C, 30 min	39	131, 132
	15e	$AsPh_3$		**15a**, $AsPh_3$, $NaBPh_4$, CH_2Cl_2, 20 °C, 30 min	41	132
	15f	$SbPh_3$		**15a**, $SbPh_3$, $NaBPh_4$, CH_2Cl_2, 20 °C, 30 min	37	132
	15h	4-MeC_5H_4N		**15a**, 4-MeC_5H_4N (1.2 equiv.), $NaBPh_4$, CH_2Cl_2 – Me_2CO, Δ, 5 h	34	132
	15i [c]	PPh_2Me		**15a**, PPh_2Me, $NaBPh_4$, CH_2Cl_2 – $Me_2^{\circ}O$, 20 °C, 30 min	54	132
	15j	PCy_3		**15a**, PCy_3, $NaBPh_4$, CH_2Cl_2 – $Me_2^{\circ}O$, 20 °C, 30 min	32	131, 132
	15m	$P(OMe)_3$		**15a**, $P(OMe)_3$, $NaBPh_4$, CH_2Cl_2 – $Me_2^{\circ}O$, 20 °C, 30 min	23	132
	15n	3,5-dmpz		**15a**, 3,5-dmpz, $NaBPh_4$, CH_2Cl_2 – $Me_2^{\circ}O$, 20 °C, 30 min	24	132
	**15g**			**15a**, 4-MeC_5H_4N (4.2 equiv.), $NaBPh_4$, CH_2Cl_2 – Me_2CO, 20 °C, 30 min	14	132
	**35b** [c]	PPh_3		**35a**, PPh_3, $NaBPh_4$	–	136
	35c	PPh_2Me		**35a**, PPh_2Me, $NaBPh_4$	–	136
	35d	$AsPh_3$		**35a**, $AsPh_3$, $NaBPh_4$	–	136
Five-membered palladacycles						
	**16e**	PPh_3		**16d**, PPh_3, $NaBPh_4$, CH_2Cl_2, 20 °C, 30 min	33	131, 132
	16f	PCy_3		**16d**, PCy_3, $NaBPh_4$, CH_2Cl_2, 20 °C, 30 min	20	131, 132

Supplement 2 (continued).

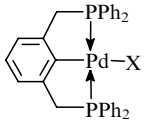
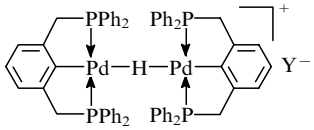
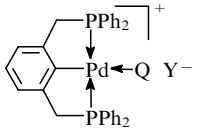
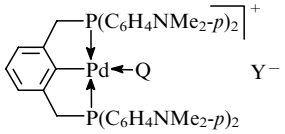
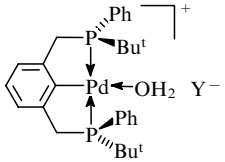
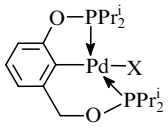
Complex	Number of the compound	Q	X	Starting complexes,[a] reagents and reaction conditions	Yield (%)[c]	Ref.
Five-membered palladacycles						
	**16b**[c,d]		I	**16a**, KI, Me_2CO, Δ, 4 h	62	133
	16i[c,d]		SCN	**16a**, KSCN, Me_2CO, Δ, 4 h	73	133
	**16j**[c,e]		SCN	$[(C_6Cl_5)ClPd(\eta^2\text{-}L^{16})]$, KSCN, Me_2CO, Δ, 4 h	71	133
	16k[c,f]		I	$[(C_6Cl_5)ClPd(\eta^2\text{-}L^{16})]$, KI, Me_2CO, Δ, 4 h	62	133

[a] The complexes $[Pd(\eta^2\text{-}L)X_2]$ or $[ArPd(\eta^2\text{-}L)X]$ were used as the starting compounds. [b] The complex exists in solutions as a 2 : 1 mixture of isomers with N- and S-bonded anions. [c] The complex exists in solutions as a mixture of *cis*- and *trans*-isomers. [d] The ratio *trans*(C,C) : *cis*(C,C) = 4 : 1. [e] The ratio *trans*(C,C) : *cis*(C,C) = 8 : 1. [f] Mixture *trans*(C,C) : *cis*(C,C) = 3 : 1.

Supplement 3. Derivatives of pincer PCP complexes.

Complex	Number of the compound[a]	Q	X	Y^-	Starting complexes,[b] reagents and reaction conditions	Yield (%)[c]	Ref.
Five-membered palladacycles annelated at the $C(sp^3)-Pd$ bond							
	**39a**		H		$[(\eta^3\text{-}L^{39})PdCl]$, $LiAlH_4$, THF, 20 °C, 4 h	75	248
	39b*		Me		$[(\eta^3\text{-}L^{39})PdCl]$, Et_2O, MeLi, 20 °C, 1 h	84	248, 255
	**39c***	H_2O			1. *a*) $[(\eta^3\text{-}L^{39})PdCl]$, Et_2O, MeLi, 20 °C, 1 h; *b*) $[Et_2NH_2]BPh_4$ (1 equiv.), moist ethylene atmosphere, 3 min;	53	248
					2. *a*) $[(\eta^3\text{-}L^{39})PdCl]$, Et_2O, MeLi, 20 °C, 1 h; *b*) $[Et_2NH_2]BPh_4$ (1 equiv.), $CD_2Cl_2-H_2O$ (~1 : 1)	~100	248
	39d	CD_3CN			*a*) $[(\eta^3\text{-}L^{39})PdCl]$, Et_2O, MeLi, 20 °C, 1 h; *b*) $[PhNH_3]BPh_4$ (1 equiv.), CD_3CN (excess)	see[d]	312
	**65**[c]				$[(\eta^3\text{-}L^{65})PdCl]$, NaI, THF, 20 °C, 2 h	93	313
Five-membered palladacycles annelated at the $C(sp^2)-Pd$ bond							
	**66b***		Ph		$[(\eta^3\text{-}L^{66})PdOC(O)CF_3]$, PhLi	81	305
	66c		I		*a*) $[(\eta^3\text{-}L^{66})PdOC(O)CF_3]$, PhLi; *b*) PhI	(~100)[d]	305
	**38a**		H		$[(\eta^3\text{-}L^{38})PdCl]$, EtOH, $NaBH_4$, Δ, 1.5 h	96	247
	38b		I		1. *a*) $[(\eta^3\text{-}L^{38})PdCl]$, $NaBH_4$, EtOH, Δ, 1.5 h; *b*) *p*-$MeOC_6H_4I$	(~100)[d]	305
					2. $[(\eta^3\text{-}L^{38})Pd(TFA)]$, LiI	–	305
	38c		C≡CPh		$[(\eta^3\text{-}L^{38})PdCl]$, HC≡CPh, Bu^nLi, PhH, Δ, 4 h	93	247
	**38d**	d_8-THF			$[(\eta^3\text{-}L^{38})PdCl]$, $AgBF_4$, d_8-THF	(>95)	253
	38e*	H_2O			$[(\eta^3\text{-}L^{38})PdCl]$, $AgBF_4$, d_8-THF, traces H_2O, 20 °C, 15 min	–	253

Supplement 3 (continued).

Complex	Number of the compound [a]	Q	X	Y^-	Starting complexes,[b] reagents and reaction conditions	Yield (%) [c]	Ref.
Five-membered palladacycles annelated at the $C(sp^2)-Pd$ bond							
	**40b**		H		$[(\eta^3\text{-}L^{40})Pd(HNMe_2)]OTf$,[e] $LiNCy_2$ (excess), d_8-THF, −78 °C	see [d]	251
	40n		NMe_2		$[(\eta^3\text{-}L^{40})Pd(HNMe_2)]OTf$,[e] $LiNCy_2$ (1 equiv.), d_8-THF, −78 °C, 2 h	see [d]	251
	40f		OMe		*a*) **40c**, $AgBF_4$, THF, 20 °C; *b*) NaOMe, THF, 10 min	–	256
	40j*		α-furyl (α-C_4H_3O)		**40i**, η^2-2-$Bu_3SnC_4H_3O$ (excess), Me_2CO (anhydrous), cooling	100	260
	40k		OH		*a*) **40c**, $AgBF_4$, THF, 20 °C, 2 h; *b*) NaOH, H_2O, 20 °C, 12 h	–	256
	40l		$O(CH_2)_4CH=CH_2$		*a*) **40c**, $AgBF_4$, *b*) $LiO(CH_2)_4CH=CH_2$, THF, 1 h	–	256
	**40a**			OTf	1. *a*) **40c**, $AgCF_3SO_3$, Me_2CO, 30 min; *b*) NaO_2CH (excess) MeOH, 30 min	~100	250
					2. $[(\eta^3\text{-}L^{40})Pd(HNMe_2)]OTf$,[e] $LiNCy_2$ (10 equiv.), THF, −78 °C, 2 h	15	251
	40m [f]			BPh_4	**40a**, $Na[BPh_4]$, MeOH	–	250
	**40d***	$PhNH_2$		BF_4	*a*) **40c**, $AgBF_4$, THF, 1 h; *b*) nb,[g] $PhNH_2$, 12 h	70–82	256
	40e	nb [g]		BF_4	*a*) **40c**, $AgBF_4$, CH_2Cl_2, 20 °C, 20 min; *b*) nb,[g] 10 min		256
	40g	PEt_3		BF_4	*a*) $[(\eta^3\text{-}L^{40})Pd(MeCN)]BF_4$, $[Pd(MeCN)_4](BF_4)_2$, THF–MeCN, 20 °C, 12 h; *b*) PEt_3, 20 °C, 2 h	64	259
	40h	THF		BF_4	**40c**, $AgBF_4$, THF, 20 °C, 20 min	–	256
	40o	Me_2CO		OTf	**40c**, AgOTf, Me_2CO, 30 min	–	250
	40p	CH_2Cl_2		BF_4	**40c**, $AgBF_4$, CH_2Cl_2, 20 °C	–	256
	**41a**	THF		PF_6	$[(\eta^3\text{-}L^{41})PdCl]$, $TlPF_6$, THF, 20 °C, 20 min	see [d]	256
	41b	nb [g]		PF_6	*a*) $[(\eta^3\text{-}L^{41})PdCl]$, $TlPF_6$, THF, 20 °C, 20 min; *b*) nb,[g] THF	see [d]	256
	41c	THF		BF_4	$[(\eta^3\text{-}L^{41})PdCl]$, $AgBF_4$, THF, 20 °C, 20 min	see [d]	256
	41d	CH_2Cl_2		BF_4	$[(\eta^3\text{-}L^{41})PdCl]$, $AgBF_4$, CH_2Cl_2	see [d]	256
	**67a**			OTf	$[(\eta^3\text{-}L^{66})PdBr]$, AgOTf, Me_2CO-H_2O, 20 °C, 1 h	95	314
	67b			BF_4	$[(\eta^3\text{-}L^{66})PdBr]$, $AgBF_4$, Me_2CO-H_2O, 20 °C, 1 h	–	314
	**37b**		I		**37a**, NaI, Me_2CO	–	246
	37c		OAc		**37a**, AgOAc, Et_2O, ultrasound	–	246

[a] The complexes studied by X-ray diffraction are asterisked. [b] The formula or the number of the starting complex is given. [c] The yield based on spectroscopic data is given in parentheses. [d] The complex was identified on the basis of spectroscopic data. [e] The synthesis of $[(\eta^3\text{-}L^{40})Pd(HNMe_2)]OTf$ has been reported.[258] [f] The complex is unstable and decomposes in solutions to give Pd(0). [g] nb is norbornene.

* * *

During the preparation of this manuscript for publication (2004–2005), a number of new studies dealing with this subject have appeared. A series of reviews on the chemistry of palladacycles [315] and their use in catalysis [316–320] published during this period demonstrates the persistent interest in this field of knowledge. Studies on the activation of C–H bonds,[321] estimation of the phosphine basicity [322] and coordination properties [323] have continued; new data on the STE of coordination [324] and organometallic [325] palladium compounds have appeared.

As regards the design of new phosphapalladacyclic structures, attention has been focused on pincer PCP-complexes. Methods for the synthesis of new CPCs of this type have been developed;[326–332] in particular, the first complexes with the ferrocenyl core [330, 331] and non-symmetric PCP′-structures with two different palladacycles were obtained.[332] The linear and branched bi- and trinuclear compounds with two or three PCP fragments [333] have been synthesised (for platinum, a tetra-PCP complex with the

porphyrin core has been prepared [334]). The unsuccessful attempt at cyclopalladation of diphosphine with the *m*-terphenyl core [335] emphasises once again the lack of stability for systems with two annelated seven-membered palladacycles.

The range of monocyclic PC-structures has been barely extended.[336, 337] The development of a new method for the synthesis of mixed-ligand *spiro*-complexes [338] and the study of the rotation isomerism of PC-palladacycles [339] deserve attention.

The works dealing with reactions of phosphapalladacycles remain scarce. Of obvious interest are the results obtained in a study of the transformations of PCP-complexes under the action of reducing agents.[340] Further development of the chemistry of CPCs would be facilitated by the use of mass spectrometry. The potential of this method has recently been demonstrated in relation to the reactions of PCP-complexes with compounds of other metals (Pt, Au, Hg).[326] New derivatives of both known and new CPCs of the PC [336, 341] and PCP types [326, 331, 342, 343] have been synthesised, in particular, unusual dimers with a bridging anion (Cl^-, CN^-, COO^{2-}) or a diphosphine linking two PCP-fragments.[326, 331, 342, 343] A derivative of the ferrocenyl PCP-complex with a monodentate borohydride ligand has been isolated and studied by X-ray diffraction. This compound is unusual not only for a CPC but also for the coordination chemistry of palladium as a whole.[331, 342] Study of the electrochemical behaviour of ferrocenyl PCP-complexes has shown oxidation of the ferrocenyl fragment.[331] The carbonylation of the hydroxy derivatives of PCP-complexes results in CO insertion into the Pd—O bond to give μ-COO dimers.[343] The main impetus for the development of the chemistry of phosphapalladacycles is still the design of new efficient homogeneous (pre)catalysts based on the PC- [336, 337, 344, 345] and PCP-type [333, 346–351] CPCs. Recently, a soluble PC-palladacycle immobilised on polystyrene has been obtained.[345]

In conclusion, note the synthesis of new phosphapalladacyclic structures containing a carbene carbon atom instead of the carbanionic atom present in the classical CPCs.[352] The first imidazol-2-ylidene ligand functionalised by a phosphine fragment was synthesised in 2002.[353] A dozen palladium complexes with chelating carbene P⁀C:-ligands have now been reported;[354–357] at least three pincer complexes with tridentate carbenes of the P⁀C:⁀P type have been obtained.[357–359] In all cases, the chelate carbene complexes were meant for being tested in catalysis; the brillian future of this line of research is beyond doubt.

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