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Jean-Michel Camus, Patricia Roy García, Jacques Andrieu, Philippe Richard, Rinaldo Poli. Resolution of β -aminophosphines with chiral cyclopalladated complexes. *Journal of Organometallic Chemistry*, 2005, 690 (6), pp.1659-1668. 10.1016/j.jorganchem.2005.01.023 . hal-03278295

HAL Id: hal-03278295

<https://hal.science/hal-03278295v1>

Submitted on 6 Jul 2021

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Resolution of β -aminophosphines with chiral cyclopalladated complexes

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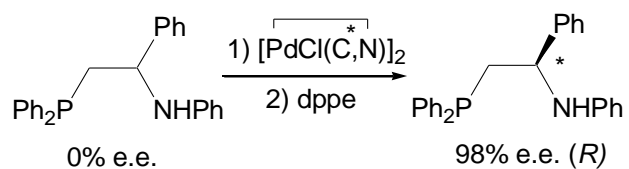
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Key words :

Aminophosphines, P,N ligands, racemic resolution, chiral palladium complexes, X-ray structures

Pictogram for contents page



Synopsis for contents page

A chiral β -aminophosphine has been isolated by resolving its racemic mixture with a palladacycle complex chiral agent. Its absolute configuration has been determined from the X-ray structure analysis of the related palladium dichloride complex.

Abstract

Resolution of the racemic chiral β -aminophosphines $\text{Ph}_2\text{PCH}_2\text{CH}(\text{Ph})\text{NH}(\text{Ar})$ (\mathbf{L}^1 for $\text{Ar} = \text{C}_6\text{H}_5$ and \mathbf{L}^2 for $\text{Ar} = 2,6\text{-C}_6\text{H}_3\text{iPr}_2$) has been investigated by use of different cyclopalladated complexes as chiral agents. The resulting complexes afford diastereomeric adducts in a 1:1 ratio. After successive crystallizations from ethanol, a d.e. of 98% was achieved for one amino-phosphine palladium complex, while no significant d.e. was obtained after crystallizations from chlorinated solvents. The X-ray structure analysis has pointed out intermolecular hydrogen interactions $\text{N-H}\cdots\text{Cl}$ between the P,N ligand and the chloride ion, which are responsible for the formation and stabilization of the diastereomeric adducts. Thus, the use of oxygenated solvents cancels such hydrogen interactions by their stronger donor character and makes the diastereomers separation possible, allowing to isolate the optically pure (*R*)- $\text{Ph}_2\text{PCH}_2\text{CH}(\text{Ph})\text{NH}(\text{Ph})$ \mathbf{L}^1 of which the absolute configuration has been determined from the X-ray structure analysis of the related palladium dichloride complex.

Introduction

Since the last decade, P,N ligands, specifically amino-phosphines, have found numerous applications in the field of homogeneous catalysis with catalysts based on Pd^1 , Pt^2 , Ru^3 , $\text{Rh}^{1,4}$ or Ir^5 . In addition, chiral versions of these ligands exhibit interesting properties in asymmetric catalysis. For instance, the selective P,N chelation by the chiral phosphinediamine (*S,S*)- $[\text{iPrP}\{o\text{-C}_6\text{H}_4\text{-CH}(\text{CH}_3)\text{N}(\text{CH}_3)_2\}_2]$ induces an effective chiral field in a rhodium complex leading to high enantioselectivities in acrylic acid hydrogenation.⁴ As another example, the nature of the N-substituent of other amino-phosphines chelates (*S*)- $[\text{Ph}_2\text{CH}_2\text{CH}(\text{iPr})\text{NR}^1\text{R}^2]$ (with $\text{R}^1 = \text{Me}$ or Ph and $\text{R}^2 = \text{Ph}$ or iPr) affects the enantioselectivity in palladium-catalysed allylic alkylation.⁶

Generally, the synthesis of achiral amino-phosphines involves one or two steps⁷⁻⁹. In the same way, the racemic chiral β -amino-phosphines \mathbf{L}^1 and \mathbf{L}^2 are also obtained in one step by reaction between the $\text{Ph}_2\text{PCH}_2^-$ anion and imines¹⁰, see Chart 1.

<Insert Chart 1>

Nevertheless, the extension to the preparation of chiral β -amino-phosphines in an enantiomerically pure form requires long and tedious steps in order to introduce a stereogenic center in a defined absolute configuration. The different strategies are based either on the use of chiral amino-acids or L-valine¹¹⁻¹³ as starting chiral compound, or on the use of a chiral saturated N-

heterocycle,¹⁴ or again on stereoselective additions to optically pure imines¹⁵ or substituted aziridines¹⁶. These multistep syntheses lead to a single enantiomer of the similar ligands Ph₂PCH₂CH(ⁱPr)NPh₂¹², Ph₂PCH₂CH(ⁱPr)NHⁱPr and Ph₂PCH₂CH(ⁱPr)NH₂⁶ from L-valinol (derived from L-Valine by reduction), with global yields between 17 and 25%. The access to both ligands **L**¹ and **L**² in an optically pure form in a shorter way than those mentioned above and/or by another higher yield procedure would be desirable for application to enantioselective catalytic processes.

With specific reference to palladium catalyzed asymmetric allylic allylation, we have recently studied the cationic complexes [Pd(η³-CH₂CHCHR){Ph₂PCH₂CH(Ph)NH(Ar)-κ²-P,N }]⁺ (with R = Me, Ph, Ar = Ph, 2,6-C₆H₃ⁱPr₂) and reported that the change of N-substituent modifies significantly the *endo/exo* ratio without changing the *trans-P/cis-P* ratio when R = Me. For the phenylallyl Pd(II) complexes, on the other hand, the opposite phenomenon was observed (see Scheme 1)¹⁷. Under the assumption that the *exo* and *endo* isomers react at the same rate with a nucleophile, the *endo/exo* ratio could then allow to control the enantioselectivity during the nucleophile addition, when using enantiomerically pure versions of the chiral amino-phosphine ligand.

<Insert Scheme 1>

In addition to the above mentioned asymmetric syntheses, optically pure P,N ligands can also be obtained by racemic resolution via specific resolving agents. The phosphorus atom has basic properties, but the general organic methods employing tartaric or camphrosulfonic acid cannot be applied because of its air sensitivity. A specific procedure for the resolution of tertiary phosphines¹⁸⁻²⁰ di-phosphines^{21,22} or hydroxy-phosphines^{23,24} is based on the use of an optically active palladium metallacycle complex, which is available on a gram scale, as chiral agent. We wished to extend this procedure to heteroditopic ligands like the amino-phosphines **L**¹ and **L**² and report herein the results of our studies.

Results and discussion

Synthesis of neutral amino-phosphines palladium complexes

The reaction of the chiral chloro-palladium dimer (*S*)-**1** (prepared by orthometallation of (*S*)-methylbenzylamine by Pd(acetate)₂²⁵) with two equivalents of **L**¹ or **L**² leads to complexes **2** and **3**, respectively, as a mixture of two diastereomers labelled "a" and "b" (see Scheme 2).

<Insert Scheme 2>

The ^{31}P -NMR spectrum shows the presence of two singlets with equal intensity at $\delta = 40.45$ and at 40.67 ppm for **2^{a,b}** (and at $\delta = 38.73$ and at 38.51 ppm for **3^{a,b}**). The 1:1 diastereomeric ratio was also confirmed by ^1H -NMR integration of N-methyl protons, which is an excellent probe because the chemical shifts for the two diastereomers differ by 0.3 ppm and there is no overlap with others protons of the complex.

Separation of the diastereoisomers

The first attempt to separate the diastereomers of **2** and **3** consisted in the use of chromatographic column over silica gel. Different solvent mixtures were tried, but none of them proved suitable. Subsequently, we attempted fractional crystallizations. Yellow crystals of **2** were obtained from a CH_2Cl_2 /pentane mixture. Their analysis by ^1H and ^{31}P NMR spectroscopy indicated the presence of a 1:1 mixture of the two diastereoisomers, revealing no d.e. for the crystallization process.

One of the crystals of **2** was investigated by X-ray diffraction. The crystal data and structure refinement parameters are given in Table 1. The unit cell is non centro-symmetric (space group P2_1) due to the presence of a single enantiomer for each diastereomer. The asymmetric unit contains the two molecules **2^a** and **2^b**, linked to each other by hydrogen bonding, in a 1:1 ratio. An ORTEP view (see Figure 1) shows the κ^1 -P-coordination by the amino-phosphine ligand **L¹**. The geometry around the palladium metal center is slightly distorted square planar, with a *trans* arrangement of the nitrogen atom from the benzylamine moiety and the phosphorus atom, similar to what was already observed in $[\text{PdCl}\{\text{PPh}(\text{iPr})(\text{OMe})\}(\text{C},\text{N})]$ (with C,N = (*R*)-{(1-(dimethylamino)ethyl}-2-naphthalenyl).²⁶

<Insert Figure 1 and Table 1>

The five-membered metallacycles adopt an envelope conformation with the N(1) and N(1)* atoms at the flap. The bond lengths within the ortho-metallated benzylamine chelate (see Table 2) are quite similar to those found in similar palladium complexes containing other tertiary phosphines.^{19,26}

<Insert Table 2>

The more interesting feature of this structure, however, concerns the dangling NPh groups of the P,N ligand in both diastereomers, which are involved in intramolecular N-H...Cl hydrogen interactions. Indeed, the separations between the Cl and N atoms (Cl-N(2), 3.284(7) Å; Cl*-N(2)*, 3.312(6) Å) are lower than the sum of the NH length and the van der Waals' radii of hydrogen and chloride atoms.²⁷ This is consistent with similar intramolecular interactions that we have previously reported for a α -aminophosphine rhodium complexes²⁸ and for a β -aminophosphine palladium complex,¹⁰ and that have been described by other authors for a platinum complex [PtBr-(C₆H₄CH(Me)NMe₂- κ^2 -C,N)(C₆H₄CH(Me)NHMe₂- κ^1 -C)].²⁹ In addition, the Cl and Cl* chloride atoms are also involved in intermolecular N-H...Cl interactions with the coordinated NH group of the diastereomeric partner [N(1)...Cl*, 3.426(4) Å; N(1*)...Cl, 3.629(4) Å], see Figure 1 and Table 2. Consequently, hydrogen interactions with chloride atoms are, at the same time, intra- and inter-molecular in the solid state.

In order to establish whether the N-H...Cl-Pd interactions are maintained in solution, we have recorded IR spectra for the free ligand and for the complex in solution and in the solid state. In Nujol, the NH absorption bands were found at 3390 cm⁻¹ (for the free ligand) and at 3333 and 3322 cm⁻¹ (for complexes **2^{a,b}**). These absorptions are shifted to 3424 cm⁻¹ for the free ligand (in CH₂Cl₂) and to 3327 and 3317 cm⁻¹ for complexes **2^{a,b}** (in CHCl₃). In addition, dilution of the CHCl₃ solution of **2^{a,b}** by a factor of ten does not yield any shift for the NH absorption bands. These IR observations clearly show that the hydrogen interactions that are present in the solid state are also maintained in solutions of chlorinated hydrocarbons for the Pd complexes, contrary to the free ligand. This suggest that the separation of the diastereomers in chlorinated solvents is probably impossible. On the other hand, solutions in THF yielded NH bands at 3302 cm⁻¹ and at 3358 cm⁻¹ for the free ligand and for complexes **2^{a,b}**, respectively. The higher wavenumber of the NH absorption band for the Pd complexes suggests that the intermolecular N-H...Cl-Pd hydrogen interactions are replaced by other ones of type N-H...O with the oxygenated solvent. Since the polar solvent seems to inhibit the hydrogen interactions between diastereomers by its stronger donor character, we have decided to crystallize the complexes **2** and **3** in another Lewis base oxygenated solvent. Indeed, crystallization of **2** from hot ethanol yields a diastereomeric excess for the recovered solid. The white powder crushed out from a first crystallization revealed (by ¹H and ³¹P NMR) a 70/30 ratio, i.e. a diastereomeric excess of 40%. This crystallization procedure was repeated and the diastereomeric enrichment for the isolated product was checked by ³¹P{¹H} NMR after each crystallization, see Figure 2.

<Insert Figure 2>

After three successive crystallizations, an essentially pure diastereomer (labelled arbitrarily as **2^a**) was isolated (see Scheme 3) and characterized by a $^{31}\text{P}\{^1\text{H}\}$ singlet resonance at 40.45 ppm and by a ^1H doublet resonance at 1.59 ppm for the N-methyl protons. Since the second diastereomer was not detected in the ^1H and $^{31}\text{P}\{^1\text{H}\}$ NMR spectra, and since the commercial (*S*)-1-methylbenzylamine is at 98% e.e., the diastereomeric excess of the isolated complex is estimated at least equal to 98%. The resulting solutions from the crystallizations were evaporated and analyzed by NMR, but unfortunately they always contain significant amounts of both diastereomers. Thus, this method only allows the isolation of one diastereomer with a modest yield of 24% (relative to the corresponding **L¹** enantiomer) or 12% (relative to the **L¹** racemic mixture). However, the modest yield is comparable to those reported for some multi-step enantio- or diastereo-selective syntheses of chiral P,N ligands (see Introduction).

<Insert Scheme 3>

It is interesting to note that the ancillary C,N ligand plays also an important role in diastereomers resolution. The procedure described in Scheme 2 was also used starting from (*S*)-naphthylethylamine **4²³** instead of N,N-dimethylnaphthylethylamine (*S*)-**1**, leading to the palladium complexes **5**, analogues to **2**, see Scheme 4. After three successive crystallizations in hot ethanol (or after crystallization in different solvent mixture), no d.e. has observed in the isolated product. This result contrasts with the successful use of the palladium complexes prepared from (*S*)-**4** and (*R*)-**4** to separate the PhPMe^tBu³⁰ and QUINAP³¹ enantiomers, while the analogous palladium complexes based on (*S*)-**1** had failed. The latter observation was rationalized on the basis of an increased conformational rigidity of the C,N chelate, due to the presence of the sterically more demanding QUINAP ligand.³¹ In our case, the amino-phosphine ligand **L¹** may be insufficiently sterically demanding to lock the conformations in the corresponding palladium complex.

<Insert Scheme 4>

The separation method discussed above (Scheme 3) has also been applied to complexes **3^{a,b}**. Unfortunately, the highest d.e., obtained after numerous recrystallizations, was only 57%, equivalent to a **3^a/3^b** ratio of 78/21. In order to achieve this separation, the new palladium complexes **6** and **7** have been prepared by abstraction of a chloride anion with NaPF₆ from complexes **2** and **3**, see scheme 5.

<Insert Scheme 5>

The $^{31}\text{P}\{^1\text{H}\}$ NMR spectrum of complexes **6** and **7** shows a heptuplet at -143.2 ppm for the PF_6^- anion and two singlets at $\delta = 41.32$ and 41.23 ppm (for each diastereomer of **6**) and at $\delta = 39.4$ and 39.0 ppm (for each diastereomer of **7**). The integration of the N-methyl resonances in the ^1H NMR shows that both complexes **6** and **7** are formed without d.e. Unfortunately, after crystallizations from hot ethanol, the diastereomeric enrichment did not exceed 12 and 27 %, for complexes **6^{a,b}** and **7^{a,b}**, respectively, see scheme 5.

De-coordination of optically pure ligand **L¹** and determination of its configuration

According to the literature^{23,26}, the enantiomerically enriched phosphine ligand can be released from the cyclopalladated complex by addition of one equivalent of chelating bis(diphenylphosphino)ethane (dppe) ligand and easily isolated by extraction with flash chromatography. Although the ligand can then be coordinated to any transition metal, the ortho-palladium complex can not be recovered. However, in few cases, the latter palladium resolving agent has been recycled, for example, by a ligand transmetallation process based on the formation of stronger metal-phosphorus bonds like Pt-P vs Pd-P.²³ Application of this procedure to complex **2^a**, Scheme 6, was relatively straightforward (see experimental section).

<Insert Scheme 6>

The optical purity of the free ligand **L¹** should be at 98% e.e., the same as the starting complex **2^a**, because decoordination process does not modify the absolute configuration of the carbon stereogenic centre. In order to determine the absolute configuration, two crystallizations were attempted in a CH_2Cl_2 /pentane mixture and in hot ethanol. Unfortunately, no crystals suitable for an X-ray structure analysis were obtained. Consequently, a related palladium complex **8^a** was prepared from the optically pure ligand **L¹** and $\text{PdCl}_2(\text{COD})$, following the same procedure described for the preparation of the racemic mixture of complex $[\text{PdCl}_2\{(R/S)\text{Ph}_2\text{P-CH}_2\text{CH(Ph)NHPH-}\kappa^2\text{-P,N}\}]^{10}$, see Scheme 7.

<Insert Scheme 7>

X-ray Structure Analysis of complex $[\{\text{PdCl}_2\{(\text{R})\text{-Ph}_2\text{PCH}_2\text{CH}(\text{Ph})\text{NHPh-P,N}\}] \mathbf{8^a}$

The asymmetric unit contains two independent molecules linked by two intermolecular hydrogen interactions $\text{NH}\cdots\text{Cl}$ and four CH_2Cl_2 solvate molecules. The two conformations differ only by the orientation of the P-phenyl groups. The structure shows that the ligand is $\kappa^2\text{-P,N}$ coordinated in a square planar coordination geometry for the palladium center (see Figure 3). Crystal data and structure refinement parameters are given in Table 1. The selected bond lengths and angles (see Table 3) of this complex are comparable to these reported for two other $[\text{PdCl}_2(\text{P,N})]$ complexes with $\text{P,N} = \text{Ph}_2\text{PCH}_2\text{CH}(\text{Ph})\text{NHPh}$ and $\text{Ph}_2\text{PCH}_2\text{CH}((\text{CH}_2)_{2,3}\text{SMe})\text{-NMe}_2$.^{10,32} Specifically, the Pd-P, Pd-N, Pd-Cl(1) and Pd-Cl(2) distances are very close to those reported in above mentioned complexes. The Pd-Cl(2) bond length *trans* to the P atom (2.396(2) Å) is longer than that *trans* to the N atom (Pd-Cl(1) = (2.293(2) Å) owing to the stronger *trans* influence of the P with respect to the N donor group. In contrast to the $[\text{PdCl}_2((\text{R/S})\text{-Ph}_2\text{PCH}_2\text{CH}(\text{Ph})\text{NHPh-}\kappa^2\text{-P,N})]$ racemate,¹⁰ optically pure $\mathbf{8^a}$ crystallizes in a non centrosymmetric space group (P2_1) because of the presence of only one enantiomer of ligand $\mathbf{L^1}$. The asymmetric C_1 carbon atom is found in the *rectus* configuration (see Figure 3). This solid state characterization is also useful as a reference for future separations of diastereomeric palladacycle complexes, because of the absolute chemical shift assignment in the ^{31}P and ^1H NMR spectra of compound $\mathbf{2}$ (for instance, 40.45 and 40.67 ppm for the *S,R* and *S,S* diastereomers, respectively, in the ^{31}P NMR spectrum).

<Insert Table 3 and Figure 3>

Conclusion

Resolution of the racemic chiral β -aminophosphines $\mathbf{L^1}$ and $\mathbf{L^2}$ was sought by use of different cyclopalladated complexes as chiral agents. The resulting complexes afford diastereomeric adducts in a one to one ratio and the d.e. does not change significantly after crystallizations from chlorinated solvents. However, a higher d.e. was achieved by successive crystallizations from ethanol in the case of a chloro palladium complex containing the $\text{Ph}_2\text{PCH}_2\text{CH}(\text{Ph})\text{NH}(\text{Ph})$ ligand. The X-ray structure analysis has pointed out hydrogen interactions between the P,N ligand amine function and the chloride ion of each diastereomer. These $\text{N-H}\cdots\text{Cl}$ intermolecular interactions are responsible for the formation and stabilization of the diastereomeric adducts. The use of oxygenated solvents cancels such hydrogen interactions by their stronger donor character and makes the diastereomers

separation possible, allowing to isolate the optically pure amino-phosphine (*R*)-**L**¹. Despite the gram scale availability of the racemic ligand, the enantiomerically pure aminophosphine has been obtained with a low yield, which remains yet similar to those of reported enantioselective syntheses. However, better yields and/or the second enantiomer could be obtained in principle by use of other palladacycle chiral agents. The enantiomerically enriched (*R*)-**L**¹ aminophosphine will now be tested in a variety of enantioselective catalyses such as asymmetric rhodium hydroformylation, palladium allylic alkylation or ruthenium double bond hydrogenation.

Acknowledgments

We are grateful to the Ministère de la Recherche et de la Technologie for support and for a PhD fellowship (to J.-M. C.) and the Centre National de Recherche Scientifique (CNRS) for financial support of this work.

Experimental Section

All manipulations were carried out under purified argon using standard Schlenk techniques. All solvents were dried and deoxygenated prior to use by standard methods. Standard pressure NMR measurements (¹H, ¹³C{¹H} and ³¹P{¹H}) were carried out with a Bruker DRX300 spectrometer in CDCl₃ at room temperature. The peak positions are reported with positive shifts in ppm downfield of TMS as calculated from the residual solvent peaks (¹H and ¹³C{¹H}) or downfield of external 85% H₃PO₄ (³¹P). NMR data of diastereomers **a** and **b** of complexes **2**, **3**, **5**, **6** and **7** are distinguished, respectively, by the absence and the presence of a prime index superscript for the nuclei labelled in bold italic character. All IR spectra were recorded in CH₂Cl₂ solution with a Bruker IFS 66V spectrophotometer with KBr optics and the absorption vibration bands are given in cm⁻¹. Elemental analyses were carried out by the analytical service of the L.S.E.O. with a Fisons Instruments EA1108 analyzer. The commercial compounds Ph₂PCH₂CH₂PPh₂, (*S*)-1-phenylethylamine (98% e.e.), [Pd(OAc)₂], and [PdCl₂(COD)], were used as received. The preparation of ligands Ph₂PCH₂CH(Ph)NHAr **L**¹ (Ar = Phenyl) and **L**² (Ar = 2,6-diisopropylphenyl) was previously described.^{10,17} The cyclopalladated compounds (*S*)-**4** was prepared according to literature.²³

Synthesis of [{Pd(μ -Cl)(C₆H₄CHMeNH₂- κ^2 -C,N)}₂] (*S*)-**1**

The dinuclear complex has been prepared according to literature²⁵ but its preparation has been improved and its purification step has been optimised by the following procedure. To a mixture of Pd(OAc)₂ (4.17 g, 18.6 mmol) and (*S*)-1-phenylethylamine (2.4 ml, 18.5 mmol) was added 75 ml of toluene, instead of benzene as previously described²⁵. The mixture was stirred and heated at 50°C overnight. The green solution was filtered over Celite in order to eliminate the small amount of zerovalent palladium. A solution of NaCl (2 g) in 50 ml of acetone was introduced and the resulting suspension was stirred overnight. A filtration over Celite led to an orange solution which was then evaporated, leading to a yellow solid. Instead of purifying the compound by extraction with hexane as described²⁵, it was purified by chromatography using a CHCl₃/MeOH mixture in a 100/2 ratio. Orange, yellow and brown fractions were obtained and only the orange and yellow fractions were consistent to the expected product by proton NMR. Solvent evaporation of the two last fractions led to the air stable yellow compound (*S*)-**1** (1.46 g, 30%).

Synthesis of PdCl[(*S*)-C₆H₄CH(Me)NH₂-κ²-C, N][Ph₂PCH₂CH(Ph)NHPPh-κ¹-P], (**2^{a,b}**)

The chiral palladium dimer (*S*)-**1** (1.29 g, 2.5 mmol.) and the ligand **L**¹ (1.89 g, 4.9 mmol.) were dissolved in 10 ml of CH₂Cl₂. The solution was stirred for 1 h and the solvent was then evaporated. The resulting residue was washed three times with 10 ml of pentane and dried in vacuo (1.43 g, 45 %). The product was found to contain the two diastereomers **2^a** and **2^b** in a 1:1 ratio. After three successive crystallizations in hot ethanol, the diastereomer **2^a** was isolated as white crystals (0.369 g, 12 %) with 98 % d.e. This purification procedure was repeated three times from different charges of crude product and in all cases the d.e. was at least 98%. NMR data of the isolated diastereomer **2^a**: ¹H: δ 1.59 (d, 3H, ³J_{HH}=6.7 Hz, CH-CH₃), 2.46 (s, br, 1H, exchange with D₂O, CH(CH₃)-NH), 2.82 (dt, 1H, ³J_{HH}=2.8 Hz, ²J_{HP}=²J_{HH}=14.3 Hz, PCH), 3.50 (m, 1H, PCH), 3.97 (m, 1H, NCH), 4.18 (m, 1H, CH-CH₃), 5.19 (s, br, 1H, exchange with D₂O, CH(CH₃)-NH), 6.17 (s, br, 1H, exchange with D₂O, CH(CH₃)-NH) 6.51-8.21 (m, 24H, **H**_{arom}), 9.05 (d, ³J_{HH}=11.0 Hz, exchange with D₂O, Ch(Ph)-NH). ¹³C{¹H}: δ 25.8 (CH-CH₃), 40.3 (d, 1C, ²J_{CP}=28 Hz, PCH₂), 57.6 (CH-CH₃), 66.5 (NCH), 122.4-159.8 (m, 30C, **C**_{arom}). ³¹P{¹H}: δ 40.45 (s, **P**). NMR data of the non-isolated diastereomer **2^b**: ¹H: δ 1.25 (d, 3H, ³J_{HH}=6.7 Hz, CH-CH'₃), 1.82 (s, br, 1H, exchange with D₂O, CH(CH₃)-NH'), 2.86 (dt, 1H, ³J_{HH}=2.6 Hz, ²J_{HP}=²J_{HH}=14.3 Hz, PCH'), 3.50 (m, 1H, PCH'), 3.97 (m, 1H, NCH'), 4.30 (m, 1H, CH'-CH₃), 4.58 (s, br, 1H, exchange with D₂O, CH(CH₃)-NH'), 6.51-8.21 (m, 24H, **H'**_{arom}), 9.15 (d, ³J_{HH}=10.8 Hz, exchange with D₂O, Ch(Ph)-NH'). ¹³C{¹H}: δ 25.7 (CH-C'H₃), 40.3 (d, 1C, ²J_{CP}=28 Hz, PC'H₂), 56.8 (C'H-CH₃), 66.4 (NC'H), 122.4-159.8 (m, 30C, **C'**_{arom}). ³¹P{¹H}: δ 40.67 (s, **P'**). Anal. calcd. for C₃₄H₃₄N₂PCIPd (643.5): C, 63.46; H, 5.33; N, 4.35%. Found; C, 63.15; H, 5.46; N, 4.49%.

Synthesis of PdCl[(*S*)-C₆H₄CH(Me)NH₂-κ²-C,N][Ph₂PCH₂CH(Ph)NH(2,6-C₆H₃ⁱPr₂)-κ¹-P], (**3^{a,b}**)

A mixture of (*S*)-**1** palladium dimer (1.18g, 2.25 mmol) and ligand **L**² (2.11 g, 4.53 mmol) was dissolved in 30 ml of THF. After stirring for 1.5 h, the solvent was removed and the orange residue was purified by flash chromatography over silica gel by use of a CHCl₃/isopropanol mixture in a 20/1 ratio. After solvent evaporation, the diastereomers were found in 1:1 ratio and isolated as a yellow air stable solid, which was dried in vacuo (1.18 g, 36%). In contrast to complexes **2^{a,b}**, the successive crystallizations in hot ethanol did not affected the diastereomeric excess of **3^{a,b}**. NMR data of diastereomer **3^a**: ¹H: δ 0.67 (s, br, 6H, CH-(CH₃)₂), 0.88 (s, br, 6H, CH-(CH₃)₂), 1.50 (d, 3H, ³J_{HH}=6.6 Hz, NCH-CH₃), 2.32 (s, br, 1H, exchange with D₂O, CH(CH₃)-NH^a), 2.94 (dt, 1H, ³J_{HH}=2.8 Hz, ²J_{HP}=²J_{HH}=14.7 Hz, PCH^a), 3.72 (m, 2H, CH-(CH₃)₂), 3.89 (m, 1H, NCH), 4.08 (q, 1H, ³J_{HH}=6.3 Hz, CH-CH₃), 4.35 (m, 1H, exchange with D₂O, CH(CH₃)-NH^b), 4.44 (m, 1H, PCH^b), 6.51-8.21 (m, 23H, H_{arom} and CH(Ph)-NH). ¹³C{¹H}: δ 24.4, 25.1, 25.7 and 28.6, (s, br, 4C, CH(CH₃)₂), 38.4 (d, ²J_{CP}=28 Hz, PCH₂), 57.7 (CH-CH₃), 65.6 (d, ³J_{CP}=4 Hz, NCH), 123.8-159.4 (m, 30C, C_{arom}). ³¹P{¹H}: δ 38.73 (s, P). NMR data of the second diastereomer **3^b**: ¹H: δ 0.67 (s, br, 6H, CH-(CH₃)₂), 0.88 (s, br, 6H, CH-(CH₃)₂), 1.17 (d, 3H, ³J_{HH}=6.8 Hz, NCH-CH₃), 2.32 (s, br, 1H, exchange with D₂O, CH(CH₃)-NH^a), 2.94 (dt, 1H, ³J_{HH}=2.8 Hz, ²J_{HP}=²J_{HH}=14.7 Hz, PCH^a), 3.72 (m, 1H, CH^a-(CH₃)₂), 3.89 (m, 1H, NCH^a), 4.08 (q, 1H, ³J_{HH}=6.3 Hz, CH-CH₃), 4.35 (m, 1H, exchange with D₂O, CH(CH₃)-NH^b), 4.44 (m, 1H, PCH^a), 4.52 (q, 1H, ³J_{HH}=6.3 Hz, CH^a-CH₃), 6.51-8.21 (m, 23H, H^a_{arom} and CH(Ph)-NH^a). ¹³C{¹H}: δ 24.4, 25.1, 25.7 and 28.4 (s, br, 4C, C^aH(CH₃)₂), 37.8 (d, ²J_{CP}=28 Hz, PC^aH₂), 57.6 (C^aH-CH₃), 64.3 (d, ³J_{CP}=4 Hz, NC^aH), 123.8-159.4 (m, 30C, C^a_{arom}). ³¹P{¹H}: 38.51 (s, P^a). Anal. calcd. for C₄₀H₄₆N₂PClPd (727.6): C, 66.02; H, 6.37; N, 3.85%. Found; 65.67; H, 6.31; N, 3.99%.

Synthesis of PdCl[(*S*)-C₁₂H₆CH(Me)NH₂-κ²-C,N][Ph₂PCH₂CH(Ph)NHPh-κ¹-P], (**5^{a,b}**)

The compound **5^{a,b}** has been prepared according to the same procedure described above for **2^{a,b}**, starting from the dinuclear palladium complex (*S*)-**4** (0.78 g, 1.2 mmol) and ligand **L**¹ (0.90 g, 2.4 mmol). It has been obtained as a white powder (1.38 g, 85%) without any diastereomeric excess. Successive crystallizations in hot ethanol did not increased the d.e. NMR data for **5^a** and **5^b**: ¹H: δ 1.32 (d, 3H, ³J_{HH}=6.3 Hz, CH-CH₃), 1.57 (s, br, 1H, exchange with D₂O, CH(CH₃)-NH) 1.76 (d, 3H, ³J_{HH}=6.2 Hz, CH-CH₃), 2.77 (m, 2H, PCH et CH(CH₃)-NH), 2.89 (dt, 1H, ³J_{HH}=2.8 Hz,

$^2J_{\text{HH}}=^2J_{\text{HP}}=14.2$ Hz, *PCH*), 2.96 (s, br, 2H, exchange with D₂O, 2 CH(CH₃)-*NH*), 3.56 (dt, 1H, $^3J_{\text{HH}}=3.6$ Hz, $^2J_{\text{HH}}=^2J_{\text{HP}}=14.2$ Hz, *PCH*), 3.83 (m, 2H, *NCH* et *PCH*), 4.12 (ddd, 1H, $^3J_{\text{HH}}=2.7$ Hz, $^3J_{\text{HH}}=3.6$ Hz, $^2J_{\text{HP}}=10.4$ Hz, *NCH*), 4.97 (m, 2H, 2 *CH-CH*₃), 6.95-8.33 (m, 52H, *H*_{arom}), 10.03 (d, 1H, exchange with D₂O, $^3J_{\text{HH}}=9.6$ Hz, *NH*), 10.07 (d, 1H, exchange with D₂O, $^3J_{\text{HH}}=9.7$ Hz, *NH*). ¹³C{¹H}: δ 25.2 (*CH-CH*₃), 25.9 (*CH-CH*₃), 42.2 (d, $^2J_{\text{CP}}=28$ Hz, *PCH*₂), 42.9 (d, $^2J_{\text{CP}}=29$ Hz, *PCH*₂), 55.1 (*CH-CH*₃), 56.4 (*CH-CH*₃), 66.0 (*NCH*), 67.4 (*NCH*), 122.7-155.5 (m, 68C, *C*_{arom}). ³¹P{¹H}: δ 41.01 (s, *P*), 41.37 (s, *P'*). Anal. calcd. for C₃₈H₃₆N₂PClPd (693.5): C, 65.81; H, 5.23; N, 4.04%. Found; C, 65.32; H, 5.61; N, 3.79%.

Synthesis of {Pd[(*S*)-C₆H₄CH(Me)NH₂-κ²-*C,N*][Ph₂PCH₂CH(Ph)NHPh-κ²-*P,N*]}⁺PF₆⁻ (**6^{a,b}**)

To a solution of palladium dimer (*S*)-**1** (0.75 g, 1.4 mmol) in 20 ml of CH₂Cl₂ was added a solution of ligand **L**¹ (1.08 g, 2.8 mmol) in 10 ml of CH₂Cl₂ and the mixture was stirred for 2 h. The solution was then added to a suspension of NaPF₆ (0.66 g, 3.9 mmol) in 5 ml of CH₂Cl₂ and stirred for 4 h. The resulting yellow solution was then filtered over Celite and concentrated until a precipitate appeared. This was washed three times with 30 ml of pentane and dissolved in hot ethanol. After cooling to -30°C, complex **6** was obtained as a white microcrystalline product (1.58 g, 75 %), without any d.e. (by integration of ¹H NMR spectrum). A low d.e. of 12% was obtained after two successive crystallizations in hot ethanol. NMR data for both diastereomers **6^a** and **6^b**: ¹H : δ 1.18 (d, 3H, $^3J_{\text{HH}}=6.5$ Hz, *CH-CH*₃), 1.52 (d, 3H, $^3J_{\text{HH}}=6.4$ Hz, *CH-CH*'₃), 1.78 (s, br, 1H, exchange with D₂O, *NH*), 2.51 (s, br, 1H, exchange with D₂O, *NH*), 2.90 (dt, 2H, $^3J_{\text{HH}}=3.2$ Hz, $^2J_{\text{HP}}=^2J_{\text{HH}}=14.4$ Hz, *PCH* et *PCH*'), 3.23 (dt, 2H, $^3J_{\text{HH}}=3.2$ Hz, $^2J_{\text{HP}}=^2J_{\text{HH}}=14.6$ Hz, *PCH* et *PCH*'), 3.56 (s, br, 1H, exchange with D₂O, *NH*), 3.90 (m, 2H, *NCH* et *NCH*'), 4.25 (m, 2H, *CH-CH*₃ et *CH*'-*CH*₃), 4.49 (s, br, 1H, exchange with D₂O, *NH*), 6.26 (m, 2H, exchange with D₂O, *NH*), 6.48-8.12 (m, 48H, *H*_{arom} and *H*'_{arom}). ¹³C{¹H}: δ 25.5 (*CH-C*'₃), 26.3 (*CH-CH*₃), 40.0 (d, 2C, $^2J_{\text{CP}}=28$ Hz, *PCH*₂ and *PC*'₂), 57.3 (*CH-CH*₃), 57.8 (*C*'₃-*CH*₃), 66.9 (d, 2C, $^3J_{\text{CP}}=6$ Hz, *NCH* et *NC*'₃), 122.4-157.1 (m, 60C, *C*_{arom} and *C*'_{arom}). ³¹P{¹H}: δ 41.32 (s, *P*), 41.23 (s, br, *P'*), -143.2 (h, $^1J_{\text{PF}}=715$ Hz, PF₆⁻). Anal. calcd. for C₃₄H₃₄N₂F₆P₂Pd (753.0): C, 54.23%; H, 4.55; N, 3.72%. Found: C, 54.73; H, 4.55; N, 3.87%.

Synthesis of {Pd[(*S*)-C₆H₄CH(Me)NH₂-κ²-*C,N*][Ph₂PCH₂CH(Ph)NH(2,6-C₆H₃ⁱPr₂)-κ²-*P,N*]}⁺PF₆⁻ (**7^{a,b}**)

Complexes **7^{a,b}** were prepared by the same procedure described above for complexes **6**, starting from palladium dimer (*S*)-**1** (0.58 g, 1.1 mmol), ligand **L**² (1.03 g, 2.2 mmol), and NaPF₆ (0.47 g, 2.8 mmol). They were obtained as white needles (1.31 g, 82%), without any d.e. A distereomeric

excess of 27% was obtained after two successive crystallizations in hot ethanol. NMR data for both diastereomers **7^{a,b}**. ¹H : δ 0.08 (d, 3H, ³J_{HH}=6.4 Hz, CH-(CH₃)₂), 0.17 (d, 3H, ³J_{HH}=6.4 Hz, CH-(CH₃)₂), 0.59 (d, 3H, ³J_{HH}=6.3 Hz, CH-(CH₃)₂), 0.61 (d, 3H, ³J_{HH}=6.3 Hz, CH-(CH₃)₂), 1.07 (d, 3H, ³J_{HH}=6.3 Hz, CH-(CH₃)₂), 1.08 (d, 3H, ³J_{HH}=6.2 Hz, CH-(CH₃)₂), 1.15 (d, 3H, ³J_{HH}=6.9 Hz, CH-CH₃), 1.19 (d, 3H, ³J_{HH}=6.8 Hz, CH-(CH₃)₂), 1.20 (d, 3H, ³J_{HH}=6.8 Hz, CH-(CH₃)₂), 1.48 (d, 3H, ³J_{HH}=6.8 Hz, CH-CH₃), 1.78 (m, br, 1H, exchange with D₂O, NH), 2.58 (m, 1H, exchange with D₂O, NH), 2.75 (h, 1H, ³J_{HH}=6.8 Hz, CH-(CH₃)₂), 2.77 (h, 1H, ³J_{HH}=6.6 Hz, CH-(CH₃)₂), 2.94 (dt, 1H, ³J_{HH}=3.0 Hz, ²J_{HH}=²J_{HP}=15.0 Hz, PCH), 2.95 (dt, 1H, ³J_{HH}=3.2 Hz, ²J_{HH}=²J_{HP}=15.0 Hz, PCH), 3.08 (m, 1H, exchange with D₂O, NH), 3.52 (dt, 1H, ³J_{HH}=4.7 Hz, ²J_{HH}=²J_{HP}=14.6 Hz, PCH), 3.61 (dt, 1H, ³J_{HH}=4.6 Hz, ²J_{HH}=²J_{HP}=14.5 Hz, PCH), 3.73 (h, 1H, ³J_{HH}=6.6 Hz, CH-(CH₃)₂), 3.86 (m, 2H, CH-CH₃ & NCH), 3.95 (m, 1H, NCH), 4.12 (m, 2H, CH-CH₃ and NH), 4.43 (m, 1H, CH-(CH₃)₂), 5.94 (d, 1H, exchange with D₂O, ³J_{HH}=10.9 Hz, NH), 5.96 (d, 1H, exchange with D₂O, ³J_{HH}=10.9 Hz, NH), 6.48-8.06 (m, 48H, H_{arom}). ¹³C{¹H}: δ 23.2 (1C, CH(CH₃)₂), 23.7 (1C, CH(CH₃)₂), 24.1 (1C, CH(CH₃)₂), 24.4 (1C, CH(CH₃)₂), 25.6 (1C, CH(CH₃)₂), 25.8 (1C, CH(CH₃)₂), 26.3 (1C, CH(CH₃)₂), 26.4 (1C, CH(CH₃)₂), 27.5 (CH(CH₃)₂), 27.6 (CH(CH₃)₂), 29.3 (CH(CH₃)₂), 29.4 (CH(CH₃)₂), 37.3 (d, ²J_{CP}=29 Hz, PCH₂), 37.8 (d, ²J_{CP}=16 Hz, PCH₂), 57.4 (CH-CH₃), 58.0 (CH-CH₃), 64.8 (d, ³J_{CP}=4 Hz, NCH), 65.0 (d, ³J_{CP}=4 Hz, NCH), 123.4-157.0 (m, 60C, C_{arom}). ³¹P{¹H}: δ 39.4 (s, 1P), 39.0 (s, 1P'), -143.4 (h, PF₆⁻). Anal. calcd. for C₄₀H₄₆N₂F₆PPd (837.1): C, 57.39; H, 5.54; N, 3.35%. Found: C, 57.07; H, 5.87; N, 3.30%.

De-coordination of optically pure ligand L¹

The chiral diastereomer **2^a** (369 mg, 0.5 mmol) and the ligand dppe (231 mg, 0.5 mmol) were dissolved in 15 ml of CH₂Cl₂. The resulting yellow solution was stirred for 1 h. The solvent was removed in vacuo and the crude product was purified by flash chromatography under argon over silica gel by use of a Et₂O/pentane mixture in a 1/10 ratio (R_f = 0.8). The ligand was obtained as a white powder with a 98% e.e. (175 mg, 92%). [α]_D = -28° (c = 0.41, CHCl₃). The (*R*) configuration was established from the X-ray structure of the related palladium dichloride complex **8^a**.

Preparation and crystallization of PdCl₂[(*R*)-Ph₂PCH₂CH(Ph)NHPPh-κ²-*P,N*], (**8^a**)

The preparation and the characterisation of the racemic complex [PdCl₂{Ph₂PCH₂CH(Ph)NHPPh-*P,N*}] was previously published.¹⁰ According to the procedure, complex **8^a** was synthesized from PdCl₂(COD) complex (16.6 mg, 0.06 mmol) and optically pure L¹ ligand (24.4 mg, 0.06 mmol). The mixture was dissolved in 5 ml of toluene and heated at 120°C for 1 h. The resulting yellow-green suspension was filtered and the isolated green solid was washed twice with 4 ml of pentane.

After extraction with 5 ml of CH₂Cl₂, a yellow solution was obtained, which was concentrated to half volume in vacuo. Addition and slow diffusion of a pentane layer afforded suitable yellow crystals for the X-ray analysis.

Crystal structure determination of complexes (**2^a**, **2^b**) and **8^a**

Intensity data were collected on a Nonius Kappa CCD at 110K. The structures were solved by the heavy atom method and refined by full-matrix least-squares methods³³ with the aid of the WINGX program.³⁴ Non-hydrogen atoms were anisotropically refined. Hydrogen atoms were included in calculated positions and refined with a riding model. The Flack parameters converged to 0.06(4) for **2** and 0.00(4) for **8** (respectively 0.95(4) and 1.00(4) for the inverted configurations). Crystallographic data and selected bond lengths and angles for (**2^a**, **2^b**) and **8^a** are reported respectively in Tables **1**, **2** and **3**. CCDC 258376 for (**2^a**, **2^b**) and 258377 for **8^a** contain the supplementary crystallographic data for this paper. These data can be obtained free of charge via the World Wide Web (or from the Cambridge Crystallographic Data Centre, 12 Union Road, Cambridge CB21EZ, UK; fax: (+44)1223-336-033 or emailing deposit@ccdc.cam.ac.uk).

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Table 1. Crystal data and structure refinement for palladium complexes (**2^a**, **2^b**) and **8^a**

	(2^a , 2^b)	8^a
Formula	2(C ₃₄ H ₃₄ N ₂ PCIPd)	C ₂₆ H ₂₄ NPCl ₂ Pd.2CH ₂ Cl ₂
M	1286.9	728.58
T; K	110(2)	110(2)
Crystal system	monoclinic	monoclinic
Space group	P2 ₁	P2 ₁
a; Å	11.3920(5)	12.9467(4)
b; Å	14.1080(7)	15.1518(5)
c; Å	18.1920(9)	15.8284(6)
β; °	94.623(2)	103.404(1)
V; Å ³	2914.3(2)	3024.23(18)
Z	2	4
F(000)	1320	1460
D _{calc} ; g/cm ³	1.467	1.598
diffractometer	Enraf-Nonius KappaCCD	Enraf-Nonius KappaCCD
scan type	mixture of φ rotations and ω scans	mixture of φ rotations and ω scans
λ; Å	0.71073	0.71073
μ; mm ⁻¹	0.81	1.216
Crystal size; mm ³	0.37 x 0.10 x 0.08	0.37 x 0.17 x 0.05
sin(θ)/λ max; Å ⁻¹	0.65	0.65
Index ranges	h: 0; 14 k: -16; 18 l: -23; 23	h: -16; 16 k: -18; 19 l: -20; 20
Absorption correction	SCALEPACK	SCALEPACK
RC = Refl. Collected	11674	12401
IRC = independent RC	11674	12401
IRCGT = IRC and [I>2σ(I)]	9452	9751
Refinement method	Full-matrix L.S. on F ²	Full-matrix L.S. on F ²
Data / restraints / parameters	11674 / 0 / 703	12401 / 1 / 668
R for IRCGT	R1 ^c = 0.0431, wR2 ^d = 0.0930	R1 ^c = 0.0702, wR2 ^d = 0.1658
R for IRC	R1 ^c = 0.0603, wR2 ^d = 0.1013	R1 ^c = 0.0968, wR2 ^d = 0.1815
Absolute structure parameter	0.05(4)	0.00(4)
Goodness-of-fit ^e	1.022	1.033
Largest diff. peak and hole; e.Å ⁻³	0.637 and -0.904	3.849 and -1.14 close to Pd atom

^c $R1 = \sum(|F_o| - |F_c|) / \sum|F_o|$. ^d $wR2 = [\sum w(F_o^2 - F_c^2)^2 / \sum [w(F_o^2)^2]]^{1/2}$ where $w = 1 / [\sigma^2(F_o^2) + (0.04P)^2 + 3.9P]$ for **2** and $w = 1 / [\sigma^2(F_o^2) + (0.1P)^2 + 8.9P]$ for **8** where $P = (\text{Max}(F_o^2, 0) + 2 * F_c^2) / 3$. ^e Goodness of fit = $[\sum w(F_o^2 - F_c^2)^2 / (N_o - N_v)]^{1/2}$.

Table 2 Selected bond lengths (Å) and bond angles (°) for complex (**2^a**,**2^b**)

Bond lengths:

Pd-C(1)	2.007(8)	Pd*-C(1*)	2.023(7)
Pd-N(1)	2.096(6)	Pd*-N(1*)	2.089(7)
Pd-P	2.251(2)	Pd*-P*	2.263(2)
Pd-Cl	2.420(2)	Pd*-Cl*	2.429(2)
N(1)...Cl*	3.426(4)	N(1*)...Cl	3.629(4)

Bond Angles:

C(1)-Pd-N(1)	81.3(3)	C(1*)-Pd*-N(1*)	82.9(3)
C(1)-Pd-P	99.0(2)	C(1*)-Pd*-P*	98.8(3)
N(1)-Pd-P	177.59(19)	N(1*)-Pd*-P*	177.65(19)
C(1)-Pd-Cl	168.9(3)	C(1*)-Pd*-Cl*	169.9(3)
N(1)-Pd-Cl	88.09(19)	N(1*)-Pd*-Cl*	87.60(19)
P-Pd-Cl	91.67(8)	P*-Pd*-Cl*	90.69(8)

Table 3. Selected bond lengths (Å) and bond angles (°) for complex **8^a**

Bond lengths:

Pd-N	2.117(7)	Pd*-N*	2.133(7)
Pd-P	2.198(2)	Pd*-P*	2.210(2)
Pd-Cl(1)	2.293(2)	Pd*-Cl(1*)	2.302(3)
Pd-Cl(2)	2.396(2)	Pd*-Cl(2*)	2.374(2)
N-C(1)	1.517(11)	N*-C(1*)	1.509(11)
P-C(2)	1.837(9)	P*-C(2*)	1.815(9)
C(1)-C(2)	1.536(14)	C(1*)-C(2*)	1.520(14)

Bond Angles:

N-Pd-P	85.4(2)	N*-Pd*-P*	85.7(2)
N-Pd-Cl(1)	172.8(2)	N*-Pd*-Cl(1*)	175.5(2)
N-Pd-Cl(2)	93.3(2)	N*-Pd*-Cl(2*)	93.7(2)
P-Pd-Cl(1)	88.17(9)	P*-Pd*-Cl(1*)	89.88(9)
P-Pd-Cl(2)	171.86(8)	P*-Pd*-Cl(2*)	176.31(9)
Cl(1)-Pd-Cl(2)	93.50(8)	Cl(1*)-Pd*-Cl(2*)	90.81(9)
C(1)-N-Pd	114.2(5)	C(1*)-N*-Pd*	113.0(6)
N-C(1)-C(2)	107.7(7)	N*-C(1*)-C(2*)	108.2(7)
C(2)-P-Pd	100.9(3)	C(2*)-P*-Pd*	101.3(3)

Caption for Figures

Figure 1. ORTEP view of (**2^a**,**2^b**). Thermal ellipsoids are drawn at the 50% probability level. Hydrogen atoms of phenyl groups are omitted for clarify.

Figure 2. $^{31}\text{P}\{^1\text{H}\}$ NMR spectra of the diastereomeric mixture of **2^a** and **2^b** from successive crystallizations in hot ethanol (top to bottom).

Figure 3. ORTEP view of complex **8^a**. Thermal ellipsoids are drawn at the 50% probability level. Only one molecule is shown for clarify.

Figure 1

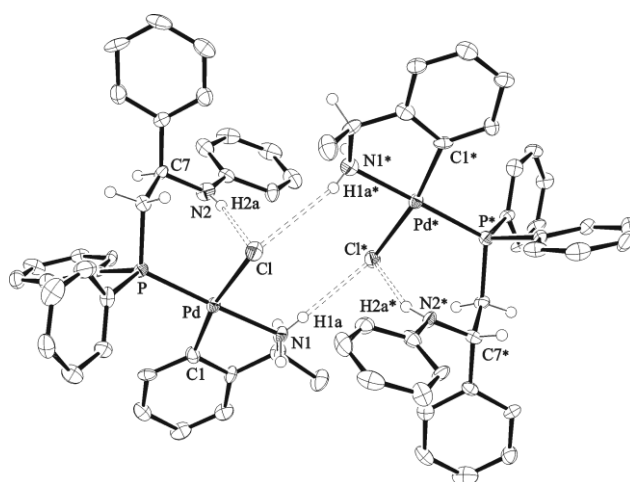


Figure 2

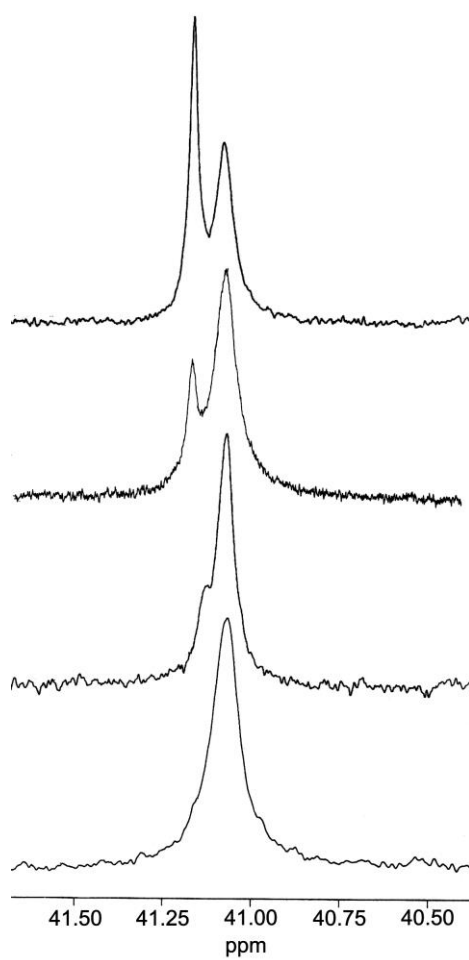


Figure 3

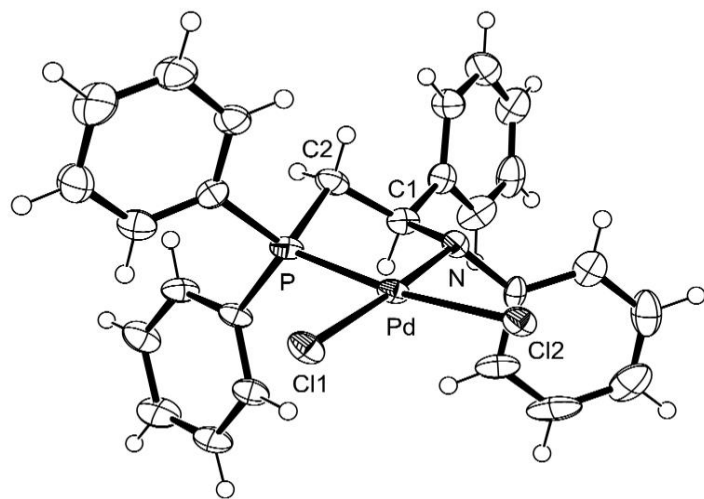
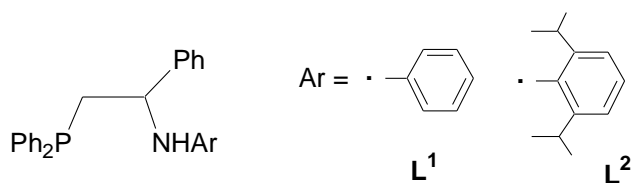
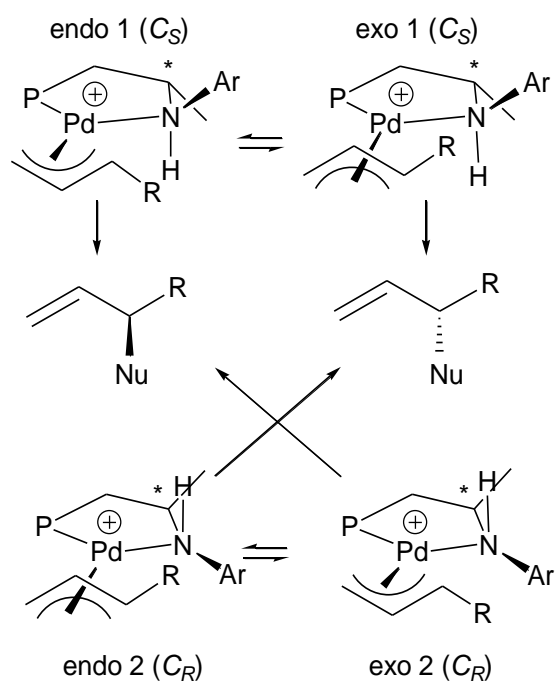


chart 1



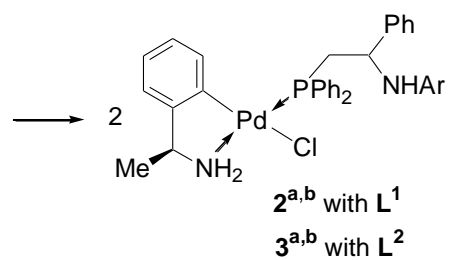
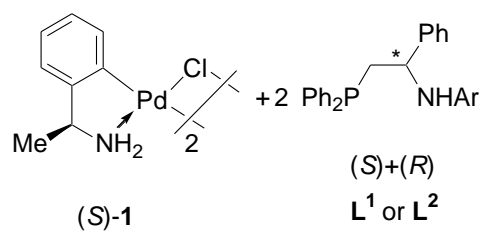
Scheme 1



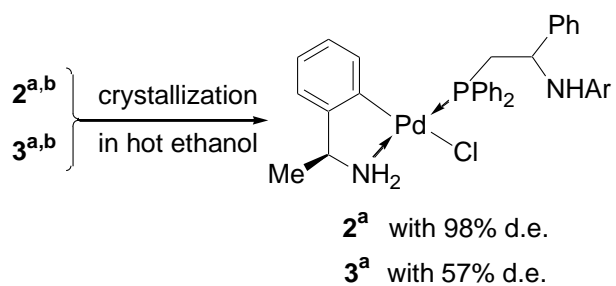
	endo/exo (enantioselectivity)		% <i>trans</i> -P isomers ^a (regioselectivity)	
R = Me	1.76 (L ¹)	8.67 (L ²)	83% (L ¹)	87% (L ²)
R = Ph	2.50 (L ¹)	1.28 (L ²)	79% (L ¹)	16% (L ²)

^a R group is in *trans* position vs P and *cis*-P isomers are omitted for clarity.

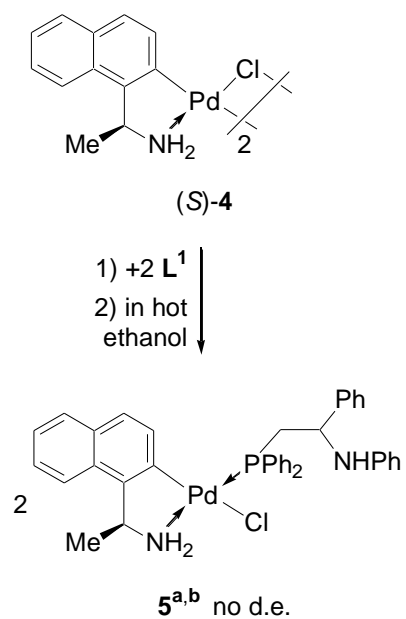
Scheme 2



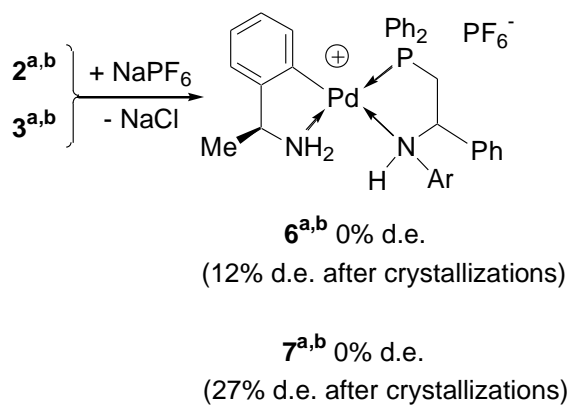
Scheme 3



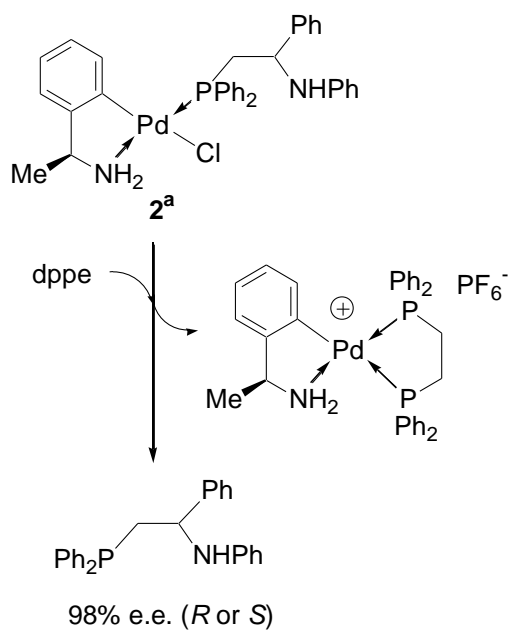
Scheme 4



Scheme 5



Scheme 6



Scheme 7

