Synthesis, Resolution, and Reactivity of Benzylmesitylphenylphosphine: A New P-Chiral Bulky Ligand

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Abstract: The synthesis of *P*,*P*′-dimesityl-*P*,*P*′-diphenyldiphosphine and benzylmesitylphenylphosphine is described as well as the resolution of the latter ligand by means of homochiral organometallic complexes. The absolute configuration of the phosphine is assigned by NMR spectra, using the homochiral palladacycle as a reference point. The configuration has been confirmed by single crystal X-ray diffraction. Molecular mechanics calculations were performed in [PdCl-(*R*)-(+)-$C_{10}H_6CH$-(Me)NH_2(PBnMesPh)], and showed that the rotation around the Pd–P bond is restricted in this complex. [Pd(η^3-2-MeC_3H_4)Cl(PBnMesPh)] was obtained and used as a precursor in the catalytic hydrovinylation of styrene. Benzylmesitylphenylphosphine has a strong tendency to form phosphapalladacycles by activation of one of the *ortho*-methyl groups. The formation of this metallacycle from cyclopalladated N-donor derivatives by a ligand-exchange reaction is also described.

Keywords: allyl ligands · asymmetric catalysis · chiral phosphines · palladium

Introduction

Transition metal complexes with chiral phosphines are widely used as catalysts in asymmetric synthesis.[1] Among the chiral phosphines developed for application in asymmetric catalysis, monodentate ligands possessing a stereogenic phosphorus atom are rare, even though asymmetric induction is expected to be improved if the stereogenic center is close to the metal atom in the catalyst.[2] In this sense, recent results on asymmetric hydrogenation or hydroformylation reactions have shown the predominance of the P-center chirality over the carbon-backbone effect.[3]

In some catalytic processes, such as the hydrovinylation reaction, the catalyst becomes inactive in the presence of bidentate phosphines, and particular attention has therefore been given to systems containing Horner phosphines ($PR^1R^2R^3$). Unfortunately, optically pure Horner phosphines are not easy to prepare.[4] Nevertheless, the synthesis and resolution of some monodentate P-chiral phosphines have been reported by using chiral resolving agents.[5] Besides this, the asymmetric synthesis of some P-chiral phosphines, $PR^1R^2R^3$, by using borane compounds has been reported,[6] through dynamic resolution of racemic *tert*-butylphenylphosphine with (−)sparteine,[7] from oxazaphospholidine complexes,[8] by reaction between Grignard reagents and phosphinates[9] or by using cyclometallated derivatives.[10]

Following our work on chiral phosphines[5f, h, 11] we describe here the synthesis, resolution and reactivity of benzylmesitylphenylphosphine, a new bulky P-chiral ligand.

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Results and Discussion

Synthesis of phosphines: We have previously reported the synthesis of (±)-benzylisopropylphenylphosphine[5h] and (±)-benzylcyclohexylphenylphosphine[5f] with high yields by using the selective cleavage of one P–CH_2Ph bond of PBn_2Ph by lithium and the subsequent reaction between the benzylphenylphosphide anion formed and isopropyl chloride or cyclohexyl bromide, respectively. When the same methodology was used in order to obtain (±)-benzylmesitylphenylphosphine, the final product of the reaction was a mixture of PBn_2Ph and PBnMesPh in an approximate ratio of (3:1). The high amount of PBn_2Ph present can be explained by a transmetallation reaction between the benzyl lithium, formed in the reaction between lithium and PBn_2Ph, and mesityl bromide, which affords benzyl bromide and mesityl lithium. The benzyl bromide formed can react with the benzylphenylphosphide, regenerating the starting material.

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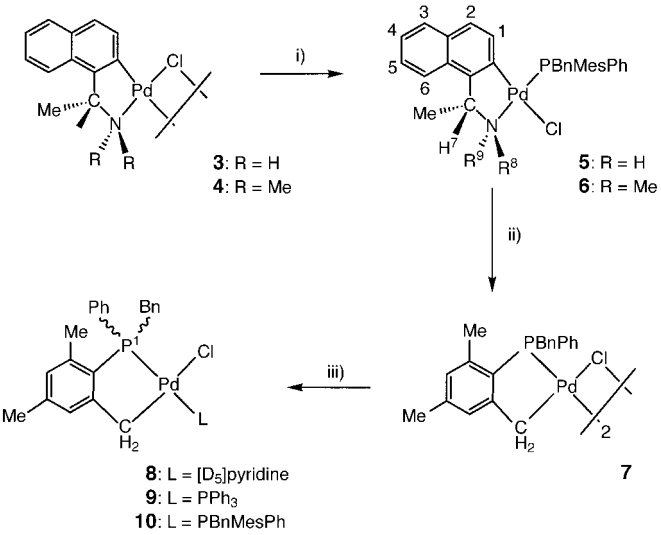
The use of diphosphines as starting materials permits an alternative approach for the synthesis of mono-phosphines, because the P–P bond is easily cleaved by treatment with lithium, yielding the lithium phosphide. The subsequent addition of an organic halide produces the corresponding mono-phosphine. The synthesis of bulky diphosphines has been reported by reaction of an excess of organolithium or Grignard reagents with chlorophosphines. The use of bulky groups prevents the cleavage of the P–P bond by further organometallic species and stabilizes the diphosphines.[12]

P,*P*′-Dimesityl-*P*,*P*′-diphenyldiphosphine was obtained as a white solid, moderately stable in air, by reaction in THF between dichlorophenylphosphine and mesitylmagnesium bromide. This diphosphine was characterized by elemental analysis and ^{1}H and ^{31}P NMR spectra. NMR data showed the presence of the two possible diastereomers in a relative ratio 1:8.

(±)-Benzylmesitylphenylphosphine was synthesized by reaction between *P*,*P*′-dimesityl-*P*,*P*′-diphenyldiphosphine and lithium metal in THF under a dry nitrogen atmosphere. After 1 h of stirring at room temperature, complete cleavage of the P–P bond of the diphosphine was accomplished, with the formation of the mesitylphenylphosphide anion. ^{31}P NMR spectra, under nitrogen, clearly illustrated the formation of this anion ($\delta = -49.38$), and these spectra were used to monitor the progress of the reaction. Subsequent addition of benzyl chloride afforded the racemic (±)-benzylmesitylphenylphosphine (**1**), in THF solution (see Scheme 1).

Resolution: *ortho*-Palladated derivatives of optically active N-donor ligands are good resolving agents for Lewis bases.[13] The optically pure cyclopalladated dinuclear compounds **3** and **4** were obtained from the optically active amines as reported.[11b, 14] Reaction of dimers **3** and **4** with benzylmesitylphenylphosphine afforded the mononuclear complexes [PdCl(C–N)(PBnMesPh)], as a 1:1 mixture of diastereomers (R_C,R_P)-**5**, **6** and (R_C,S_P)-**5**, **6** (Scheme 2).

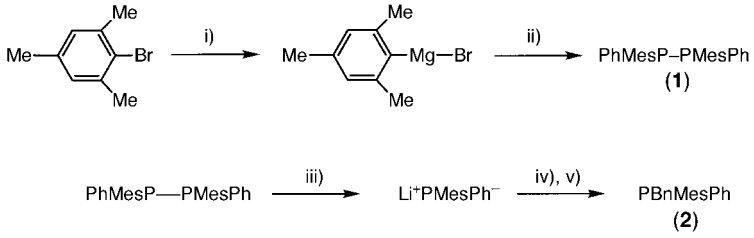
All the new organometallic compounds obtained were characterized by elemental analysis, IR spectra, and ^{1}H and ^{31}P NMR spectra. In some cases, two-dimensional NMR experiments and positive FAB-mass spectrometry were carried out to complete the characterization. The high-field shift of the aromatic protons of the metallated group in **5** and **6** due to the aromatic rings of the phosphine indicates the *cis* disposition of the phosphorus relative to the metallated carbon atom. The chemical shift of the phosphorus confirms this arrangement,[15] which is usual in cyclopalladated compounds containing phosphines.[16]



Scheme 2. i) PBnMesPh, THF, room temperature, 30 or 45 min; ii) $CHCl_3$, silica gel, room temperature, 5 d; iii) L, $CDCl_3$, room temperature.

The efficiency of cyclopalladated compounds derived from 1-(1-naphthyl)ethylamine as resolving agents has been related to the locked asymmetric envelope conformation of the metallacycle, because the methyl substituent of the chiral carbon atom adopts an axial disposition to avoid the unfavorable interaction with H^6 (see Scheme 2).[17] The NOESY spectra of both diastereomers of **5** and **6** showed that the methinic proton of the chiral carbon atom H^7 had strong negative off-diagonal peaks with H^6 and H^8 (or Me^8) and, in contrast, the methyl protons of the chiral carbon atom presented only strong NOE interaction with H^7 and H^9 (or Me^9). These data confirmed the axial disposition of this methyl group and the equatorial disposition of H^7 in these complexes.[18]

Attempts to separate the diastereomers (R_C,R_P)-**5** and (R_C,S_P)-**5** by recrystallization or column chromatography were unsuccessful and only partially enriched mixtures of these compounds were obtained. The best separation of these diastereomers was accomplished when the mixture was eluted through a silica gel column, using chloroform/acetone (100:3.5). In this case the diastereomer (R_C,S_P)-**5** was obtained in 80% yield, with a 60% *de* and the second isomer (R_C,R_P)-**5** was obtained in 32% yield, with a *de* higher than 95% (see below for the assignment of absolute configuration). Nevertheless, better results were obtained with the mixture of diastereomers **6**. The elution of this mixture in a silica gel column with $CHCl_3$/acetone (100:2) as eluent permitted the separation of the diastereomers (R_C,S_P)-**6** and (R_C,R_P)-**6** in 86 and 40% yield, respectively, with a *de* higher than 95% in both cases.



Scheme 1. i) Mg, THF, reflux, 1 h; ii) PCl_2Ph, THF, room temperature, 30 min; iii) Li, THF, room temperature, 20 min; iv) $PhCH_2Cl$, THF, 0 °C, 30 min; v) NH_4Cl, H_2O.

Assignment of the absolute configuration of phosphorus by NMR techniques: It has been demonstrated that NOE techniques[17b, 18, 19] or the NMR

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chemical shift regularities[20] can be used to determine the absolute configurations of coordinated chiral diphosphines. Dunina et al.[5g] have recently extended these studies to the monodentate P-chiral ligand *tert*-butylphenyl(4-bromophenyl)phosphine. These authors have shown that it is possible to assign the absolute configuration of this phosphine by NMR techniques using the homochiral palladacycle as a reference point.

We have shown that the rotation around the Pd–P bond is rather restricted in compounds [PdCl(C–N)(PBnRPh)] (C–N being a chiral cyclopalladated ligand and R = isopropyl or cyclohexyl group), and that this fact permits the assignment of the absolute configuration of phosphorus by NMR experiments.[5h] It is known that in all these complexes the benzyl group is separated from the metallacycle and that this group is located on the opposite side of the coordination plane in relation to the methyl group of the chiral carbon atom. In consequence, the difference between the two diastereomers is the relative position of the phenyl and R groups. In one diastereomer, the metallated ring is near to the phenyl group of the phosphine; in the other, the metallated ring is near to the group R.

In the NOESY spectra of the first eluted diastereomer of compound **6** there was a strong NOE interaction between H^1 ($\delta = 6.61$) and the methyl in the *ortho*-position of the mesityl group ($\delta = 2.64$). In contrast, in the NOESY spectra of the second diastereomer eluted of compound **6**, H^1 shows a NOE interaction with the *ortho*-hydrogen atoms of the phenyl group of the phosphine ($\delta = 7.90 - 7.97$). In conclusion, the first eluted diastereomer of compound **6** has the absolute configuration (R_C,S_P) and the second eluted diastereomer is (R_C,R_P)-**6**. In the NOESY spectra of the second eluted diastereomer of compound **5**, which contains the primary amine metallated, H^1 shows a strong NOE interaction with the *ortho*-hydrogen atoms of the phenyl group of the phosphine ($\delta = 7.88$) and, in contrast, no NOE interaction was observed with the mesityl protons, showing that this diastereomer has the absolute configuration (R_C,R_P). It should be noted that in no case was a NOE interaction observed between the CH_2P group and the metallated ring protons. The ^{31}P NMR spectrum of the solution obtained when dppe was added to the first diastereomer eluted of **6** and the free phosphine formed was treated with the cyclopalladated compound (R_C)-[PdCl($C_6H_4CHMeNH_2$)]$_2$, confirmed that the absolute configuration of the phosphine is the same in the first eluted diastereomers of **5** and **6**.

In order to estimate the height of the energy barrier corresponding to the rotation of the phosphine ligand, a coordinate driving study, based on the molecular mechanics methodology, was undertaken in compound **5**. The phosphorus – palladium bond was rotated in nine degree steps, keeping the C-Pd-Cl and N-Pd-P angles fixed at 180° and optimizing the remaining geometric parameters. Figure 1 shows the variation of the relative energy as a function of the Cl–Pd–P–C(Ph) dihedral angle, θ. There are two energy minima, corresponding to θ values of 71.9 and 288.0°; the third minimum, corresponding to 195.3°, is 8.6 kcal mol^{-1} higher in energy, due to the steric hindrance between one of the protons of the CH_2 moiety in the benzylic group of the phosphine and the hydrogen bonded to the Cl atom (Scheme 2). The maximum energy corresponds to a θ value of 60.5°. In this conformation there is a steric hindrance between the phenyl ring of the phosphine and the aforementioned hydrogen bonded to the C1 atom. The height of the rotation barrier, taken as the difference of the minimum and maximum values, is 30.2 kcal mol^{-1}, which is too high to allow the free rotation of the phosphine at room temperature, thus confirming the results obtained from NMR experiments.

Cyclometallation of phosphine by ligand exchange reaction: The formation of new compounds was observed when the mononuclear complexes **5** or **6** were eluted in a silica gel column, and the same was observed when these mononuclear derivatives were kept in solution for several weeks. Careful purification by column chromatography showed that the cyclopalladated compound [Pd(μ-Cl){(2-CH_2-4,6-$Me_2C_6H_2$)PBnPh}]$_2$ (**7**) was formed, as a 2:1 mixture of diastereomers, and in some cases the mononuclear complex [PdCl{(2-CH_2-4,6-$Me_2C_6H_2$)PBnPh}(PBnMesPh)] was also detected. When $CHCl_3$ solutions of optically pure (R_C,R_P)- or (R_C,S_P)-**6** were stirred for several days at room temperature in the presence of silica gel the formation of only one diastereomer of **7**, the major one, was observed ($\delta = 57.3$ from the $^{31}P\{^1H\}$ NMR spectrum). This result discards the possibility that the two signals in ^{31}P NMR spectra are due to geometric isomerism around the Pd_2X_2 fragment and it shows that the signal $\delta = 57.3$ corresponds to (R_P,R_P)- or (S_P,S_P)-**7** and the other signal in the ^{31}P NMR spectrum ($\delta = 57.9$) corre-

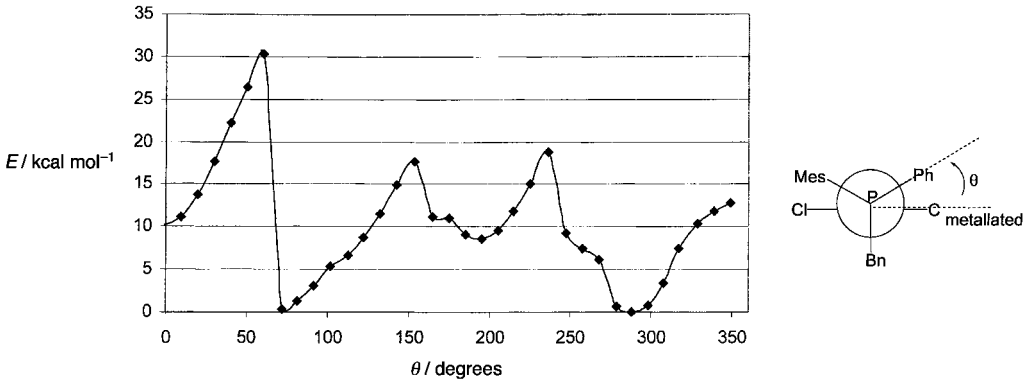
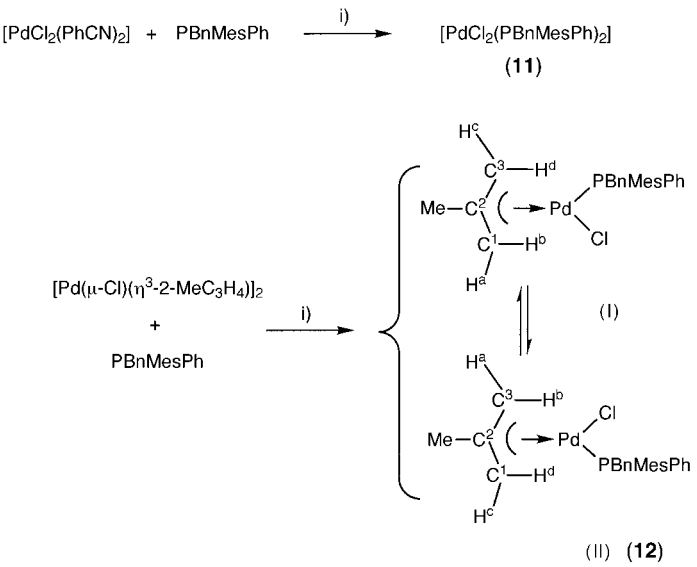


Figure 1. Variation of the relative energy of **5** as a function of the $C_{metallated}$–Pd–P–C(Ph) dihedral angle, θ.

sponds to (R_P,S_P)-**7** (the minor isomer). Compound **7** was characterized by elemental analysis, IR, ^{1}H, and ^{31}P NMR spectroscopies. The mononuclear complexes **8**, **9**, and **10** were obtained in an NMR tube by mixing 20 mg of **7** with a few drops of [D_5]pyridine or with the stoichiometric amount of triphenylphosphine or benzylmesitylphenylphosphine, respectively (see Scheme 2). All these data show that **7** is a dinuclear cyclopalladated compound obtained by regioselective activation of an *ortho*-methyl group of benzylmesitylphenylphosphine with formation of a five-membered metallacycle. It has been known, since the early work of Shaw and co-workers, that bulky phosphines undergo internal metallation with palladium and platinum centers.[21] More recently, the cyclopalladation of trimesitylphosphine by reaction between [$PdCl_2(PhCN)_2$] and $PMes_3$ has been described.[22] The synthesis of **7** from the cyclopalladated compounds **5** and **6** deserves some additional comments. This process can be considered as a ligand-exchange reaction between a metallated C–N ligand and benzylmesitylphenylphosphine, or a transcyclometallation reaction using the term recently proposed by van Koten. This reaction has been used to prepare new metallacycles and to evaluate the relative stability of these complexes.[23] Some examples of this process are known and the exchange usually takes place between two N-donor ligands,[24] although, in some cases, this reaction has been described between metallated phosphites and N-donor ligands,[25] between metallated N-donor ligands and dimetoxythiobenzophenone (with the formation of a metallated C–S ligand),[26] or between metallated *N*,*N*-dimethylbenzylamine and benzyldiphenylphosphine (with formation of a metallated C–P ligand by activation of an *ortho*-$C_{aromatic}$–H bond).[27] Recently, van Koten and co-workers have described the synthesis of the bis *ortho*-cyclometallated platinum complex [Pt(PCP)Cl] (PCP = $[C_6H_3(CH_2PPh_2)_2$-2,6$]^-$) from the cyclometallated compound [Pt(N-C-N)Cl] (NCN = $[C_6H_3(CH_2NMe_2)_2$-2,6$]^-$).[28] The reaction here described is, to the best of our knowledge, the first synthesis of a phosphapalladacycle, containing a CH_2–Pd bond, by a ligand-exchange reaction.

Synthesis of [$PdCl_2$(PBnMesPh)$_2$] and metallation of the ligand: [$PdCl_2(PBnMesPh)_2$], containing the racemic phosphine as ligand, was obtained by reaction between (±)-benzylmesitylphenylphosphine and [$PdCl_2(PhCN)_2$] in THF. After 30 min of stirring at room temperature, tetrahydrofuran was replaced by diethyl ether and [$PdCl_2${(±)-PBnMesPh}$_2$] precipitated as a 1:1 mixture of diastereomers (Scheme 3). Complex **11** was characterized by elemental analysis, IR, FAB-mass, ^{1}H, and ^{31}P NMR spectroscopies. Surprisingly, **11** was recovered in relatively low yield (approximately 40–50%) when eluted on a silica gel column with $CHCl_3$ as eluent, and the phosphapalladacycle **7**, which was not present in the sample before the column chromatography elution, was isolated from the more polar fractions. This result shows that the activation of an *ortho*-methyl group of benzylmesitylphenylphosphine, of the coordination compound **11**, took place in the column with formation of the five-membered phosphapalladacycle [Pd(μ-Cl){(2-CH_2-4,6-$Me_2C_6H_2$)PBnPh}]$_2$. This finding confirms the strong tendency of benzylmesitylphenylphosphine to afford cyclopalladated complexes.



Scheme 3. i) THF, room temperature, 30 min.

Compound **11**, containing the phosphine in optically pure form, can be obtained by the addition of dppe to a solution of one of the optically pure diastereomers **6**, in a 1:1 ratio and subsequent reaction of the free phosphine formed with [$PdCl_2(PhCN)_2$].

Synthesis of [Pd(η^3-2-MeC_3H_4)Cl(PBnMesPh)] (12), and some studies on the hydrovinylation of styrene: This compound, containing the racemic phosphine as ligand, was obtained by reaction between (±)-benzylmesitylphenylphosphine and the dinuclear allyl complex [Pd(μ-Cl)(η^3-2-MeC_3H_4)]$_2$, in toluene. Complex **12** was characterized by elemental analysis, IR, FAB-mass, ^{1}H, and ^{31}P NMR spectroscopies. NMR data show that **12** occurs in two diastereomeric forms, I and II, because of the lack of a symmetry plane in this complex (see Scheme 3). Proton NMR data of the allylic group were assigned by comparison with literature values.[29] Unusually high field shifts of H^c and H^d were observed, showing that these protons are in close proximity to aromatic phosphine rings. Two-dimensional ^{1}H NMR NOESY experiments, carried out in $CDCl_3$ solutions, permitted the unambiguous assignment of peaks in the NMR spectrum. In addition to the negative NOE cross-peaks that arise from cross-relaxation, the phase-sensitive two-dimensional ROESY experiment also shows a series of positive cross-peaks connecting the diastereomers I and II, thereby indicating that these isomers are in equilibrium in solution, see Table 1.

Table 1. Selected exchange cross-peaks (positive NOEs) for **12**.[a]

H^a (*syn*, *trans*) [4.36] ··· H^c (*syn*, *cis*) [3.12]	pseudorotation
H^a (*syn*, *trans*) [4.32] ··· H^c (*syn*, *cis*) [3.26]	pseudorotation
H^c (*syn*, *cis*) [3.26] ··· H^d (*anti*, *cis*) [2.51]	π – σ – π process
H^c (*syn*, *cis*) [3.12] ··· H^d (*anti*, *cis*) [2.27]	π – σ – π process
H^b (*anti*, *trans*) [3.34] ··· H^d (*anti*, *cis*) [2.27]	pseudorotation
H^b (*anti*, *trans*) [3.33] ··· H^d (*anti*, *cis*) [2.51]	pseudorotation

[a] In $CDCl_3$ at 20 °C; values in brackets are the proton chemical shifts. *trans* and *cis* are referred to phosphorus atom.

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These data show that the interconversion between both diastereomers occurs by the two mechanisms known for palladium allyl complexes: the $\pi-\sigma-\pi$ process and the *syn*–*syn*, *anti*–*anti* exchange (apparent allyl rotation).[29, 30]

Compound **12**, containing the phosphine in optically pure form, can be obtained by the addition of dppe to a solution of one of the optically pure diastereomers **6**, in a 1:1 ratio, and subsequent reaction of the free phosphine formed with the dinuclear allyl complex $[Pd(\mu\text{-}Cl)(\eta^3\text{-}2\text{-}MeC_3H_4)]_2$.

The X-ray structure of **12**, containing the optically pure phosphine obtained from the first diastereomer eluted of **6**, has been determined (Figure 2). This complex crystallizes in the $P2_1$ group. The absolute configuration of the phosphine

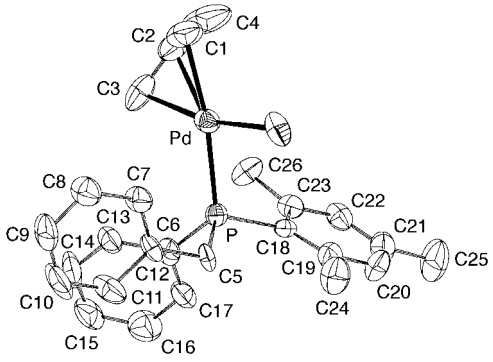

Figure 2. ORTEP plot of the structure of (*S*)-**12**.

ligand in this diastereoisomer is (*S*), confirming the assignment proposed by two-dimensional NMR techniques. The structure shows the typical geometry of an η^3-allyl bound to a transition metal and the stereochemistry around palladium is approximately square planar. Bond distances and angles are similar to those reported for related allyl compounds and the different Pd–C lengths are in agreement with the larger *trans* influence of phosphine with respect to the chloro ligand, see Table 2.[31] The dihedral angle between the plane defined by carbon atoms C1, C2, and C3, and that defined by the palladium, phosphorus, and chlorine atoms is 63.2°. The methyl group is 0.29 Å out of the plane defined by C1, C2, and C3, the other carbon atoms of the allyl ligand.

Table 2. Selected bond lengths [Å] and angles [°] for (S_P)-**12**.

Pd–C3	2.100(11)
Pd–C2	2.161(12)
Pd–C1	2.172(10)
Pd–P	2.310(2)
Pd–Cl	2.365(3)
P–C12	1.801(14)
P–C18	1.868(8)
P–C5	1.877(13)
C1–C2	1.40(2)
C2–C3	1.357(16)
C3-Pd-C2	37.1(4)
C3-Pd-C1	66.6(6)
C2-Pd-C1	37.8(6)
C3-Pd-P	105.2(4)
C2-Pd-P	136.7(4)
C1-Pd-P	170.9(4)
C3-Pd-Cl	164.1(3)
C2-Pd-Cl	130.2(4)
C1-Pd-Cl	97.8(5)
P-Pd-Cl	90.11(11)

The X-ray structure of **12**, containing racemic phosphine as ligand, has also been determined. This compound crystallizes in the $P\bar{1}$ group. The crystal structure consists of discrete molecules separated by van der Waals distances and contains the four stereomers possible.

[MCl(allyl)L] compounds (M = Ni, Pd; L = monodentate phosphine) are precursors of active species in the catalytic hydrovinylation of olefins. The hydrovinylation reaction, a codimerization process where one of the olefins is ethylene, is an attractive carbon–carbon bond formation reaction. Between the interesting characteristics of this reaction can be underlined the atomic economy of the process and the regioselectivity of the carbon–hydrogen addition observed in some subtracts.[32] Asymmetric hydrovinylation of vinyl aromatic derivatives can afford 3-phenyl-1-butene and related derivatives, which are starting materials for the synthesis of 2-arylpropionic acids, widely used as anti-inflammatory drugs such as Ibuprofen and Naproxen.[33] We have used the complex $[Pd(\eta^3\text{-}2\text{-}MeC_3H_4)(PBnMesPh)(solvent)]BF_4$, prepared in situ from **12** and $AgBF_4$ in CH_2Cl_2 solution, as a catalyst for asymmetric hydrovinylation of styrene. The results obtained are shown in Table 3. The good degree of reproducibility of the results obtained with this catalyst, and their excellent selectivity, should be pointed out. The *ee* value obtained is only moderate but it should be noted that these results were obtained at room temperature.[34]

Table 3. Hydrovinylation of styrene using $[Pd(\eta^3\text{-}2\text{-}MeC_3H_4)(PBnMesPh)(solvent)]BF_4$ as a catalyst.

Run	*T* [°C]	*t* [min]	Conversion [%]	TOF [h]	Selectivity [%]	*ee* [%]
1	15	90	39	240	96.3	
2	15	120	49	235	96.3	
3	25	45	64	770	94.5	
4	25	60	73	720	92.0	
5	25	60	80	785	87.5	
6	25	60	64	625	92.5	40(*S*)
7	25	60	61	595	94.9	40(*S*)

[a] Initial ethylene pressure 15 bar; ratio olefin/catalyst 1000:1. Catalysts were filtered solutions of **12**+styrene+$AgBF_4$, in runs 6 and 7 the catalyst contains the homochiral phosphine in their (*S*)-configuration. Conversion of the starting olefin. Selectivity of 3-phenyl-1-butene respect to the hydrovinylation fraction. TOF calculated as the total amount of arylbutenes formed. Solvent: dichloromethane, 10 mL.

Conclusion

The synthesis, resolution, and assignment of the absolute configuration and reactivity of benzylmesitylphenylphosphine, a new bulky P-chiral ligand has been described, as well as the strong tendency of this phosphine to form phosphapalladacycles by activation of one of the *ortho*-methyl groups. The formation of this metallacycle from cyclopalladated N-donor derivatives by a ligand-exchange reaction (or a transcyclometallation reaction following the term recently proposed by van Koten) is also described. To the best of our knowledge, this is the first synthesis of a P-chiral phospha-

palladacycle by this process. The extension of this reaction to the synthesis of new phosphapalladacycles, as well as the application of benzylmesitylphenylphosphine to some asymmetric catalysis processes, are currently in progress.

Experimental Section

General methods: ^{1}H NMR at 200 MHz were recorded on a Varian Gemini 200 spectrometer and ^{1}H NMR at 500 MHz, ^{13}C at 75.42 MHz, and ^{31}P{^{1}H} at 101.26 MHz were recorded on a Varian VXR 500, a Varian 300 and a Bruker DRX 250 spectrometer, respectively. Chemical shifts were measured relative to $SiMe_4$ for ^{1}H and ^{13}C and to 85% H_3PO_4 for ^{31}P. Microanalyses were performed at the Institut de Química Bio-Orgànica de Barcelona and at the Serveis Científico-Tècnics de la Universitat de Barcelona. Infrared spectra were recorded as KBr disks on a Nicolet 520 FT-IR spectrometer. The optical rotations of the complexes were determined in $CHCl_3$ at 20 °C using a Perkin–Elmer 241-MC polarimeter. Mass spectra were recorded on a Fisons VG-Quattro spectrometer. The samples were introduced in a matrix of 2-nitrobenzylalcohol for FAB analysis and then subjected to bombardment with cesium atoms. GC analyses were performed on a Hewlett–Packard 5890 Series II chromatograph equipped with a 50 m Ultra-2 cross-linked 5% phenylmethyl silicon capillary column and a FID detector connected to an HP 3396 A integrator. Mass spectra were obtained with a Hewlett–Packard 5890 Series II chromatograph equipped with the same column coupled to a Hewlett–Packard 5971 A mass selective detector. Enantiomeric excess of the hydrovinylation products was determined by GC analysis with a Hewlett–Packard 5890 chromatograph fitted with a 30 m FS-CYCLODEX column and a FID detector connected to an HP 3396 A integrator. Helium was used as a carrier gas in all cases. Conditions of analysis were: He flow: 1.30 mL min^{-1}, 80 °C; retention times: *R*-isomer, 13.43 min; *S*-isomer: 13.75 min.

Materials and synthesis: All the reactions involving free phosphines were carried out using Schlenk techniques under a nitrogen atmosphere. All solvents were dried and degassed by standard methods. Tetrahydrofuran and toluene were distilled over sodium/benzophenone, under nitrogen, before use. All chemicals were of commercial grade and used as received. Ethylene (99.95% quality) was used as received. $[Pd(\mu\text{-}Cl)(\eta^3\text{-}C_4H_7)]_2$, $[PdCl_2(PhCN)_2]$, and compounds **3** and **4** were prepared according to procedures described elsewhere.[11b, 14, 35, 36]

Synthesis of *P,P′*-dimesityl-*P,P′*-diphenyldiphosphine (1): Mesityl bromide (10.5 g, 52.5 mmol) was added to magnesium (3.5 g, 144 mmol) in tetrahydrofuran (30 mL) and the mixture refluxed for 1 h. The resulting suspension was allowed to cool at room temperature and a solution of dichlorophenylphosphine (4.3 g, 24.0 mmol) in tetrahydrofuran (30 mL) added. The resulting mixture was stirred for 30 min and hydrolyzed with an aqueous solution of ammonium chloride (15%). Afterwards, the resulting solution was washed twice with water (100 mL), the organic layer dried over anhydrous Na_2SO_4 and the solvent removed in vacuo. The addition of absolute ethanol caused the precipitation of *P,P′*-dimesityl-*P,P′*-diphenyldiphosphine as a white powder (3.9 g, 72%). ^{31}P{^{1}H} NMR (101.26 MHz, $CDCl_3$): $\delta = -34.33$ (s; minor isomer), -30.84 (s, major isomer); ^{1}H NMR (250 MHz, $CDCl_3$): $\delta = 2.16$ (s, 3H; *o*-Me major), 2.29 (s, 3H; *o*-Me minor), 2.41 (s, 3H; *p*-Me major), 2.50 (s, 3H; *p*-Me minor), 6.62 (s, 4H; aromatic Mes), 6.80–7.40 (m, 10H; aromatic); MS (positive FAB): *m*/*z*: 471 $[M+O]^+$; elemental analysis calcd (%) for $C_{30}H_{32}P_2$: C 79.28, H 7.10; found C 77.84, H 7.09.

Synthesis of (±)-benzylmesitylphenylphosphine (2): Small pieces of lithium were added to a solution of *P,P′*-dimesityl-*P,P′*-diphenyldiphosphine (2.68 g, 5.90 mmol) in tetrahydrofuran (30 mL) and the mixture stirred for 1 h at 20 °C. The excess of lithium was removed by decantating, the solution cooled to 0 °C and then an excess of benzyl chloride (3.73 g, 29.5 mmol) was added. The resulting mixture was stirred for 30 min and hydrolyzed with an aqueous solution of ammonium chloride (15%), washed twice with water (100 mL), and the organic layer dried over anhydrous Na_2SO_4. Tetrahydrofuran was removed in vacuo, and the addition of absolute ethanol caused the precipitation of benzylmesitylphenylphosphine as a white powder (2.7 g, 72%). ^{31}P{^{1}H} NMR (101.26 MHz, $CDCl_3$): $\delta = -19.7$; ^{1}H NMR (250 MHz, $CDCl_3$): $\delta = 2.20$ (s, 6H; *o*-Me), 2.26 (s, 3H; *p*-Me), 3.58 (dd, $J = 33.5$, $J = 13.1$ Hz, 1H; CH_2), 3.59 (dd, $J = 33.21$, $J = 13.3$ Hz, 1H; CH_2), 6.85 (s, 2H; Mes), 7.20–7.40 (m, 10H; aromatic); elemental analysis calcd (%) for $C_{22}H_{23}P$: C 82.99, H 7.28; found C 82.8, H 7.3.

Synthesis of [PdCl-(*R*)-(+)-$C_{10}H_6CH(Me)NH_2$)(PBnMesPh)] (5): A mixture of **3** (200 mg, 0.32 mmol) and PBnMesPh (204 mg, 0.64 mmol) in tetrahydrofuran (40 mL) was stirred at room temperature for 45 min and the resulting solution concentrated in vacuo. The solid obtained was eluted by silica gel column chromatography with $CHCl_3$/acetone (100:5) as eluent. Compound **5** (1:1 mixture of diastereomers) was isolated as a yellow solid (200 mg, 50%). ^{31}P{^{1}H} NMR (101.26 MHz, $CDCl_3$): $\delta = 11.7$ (s), 15.4 (s); MS (positive FAB): *m*/*z*: 594 $[M-Cl]^+$; elemental analysis calcd (%) for $C_{34}H_{35}NClPPd$: C 64.77, H 5.60, N 2.22; found C 64.9, H 5.5, N 2.2.

Separation of diastereomers 5: Compound **5** (200 mg) was carefully eluted at room temperature, in a silica gel column (50 g silica gel) with $CHCl_3$/acetone (100:5) as eluent. The fractions eluted (15 mL) were concentrated in vacuo and checked by ^{1}H NMR spectroscopy. The fractions of the optically pure compound (by 200 MHz ^{1}H NMR spectroscopy) were selected using the aromatic proton signals H^1. The first diastereomer eluted was (R_C,S_P)-**5** (80 mg, 80%, 60% *de*). ^{31}P{^{1}H} NMR: $\delta = 11.7$ (s); ^{1}H NMR (500 MHz, $CDCl_3$): $\delta = 1.62$ (d, J(H,H) = 6.2 Hz, 3H; Me), 2.32 (s, 3H; *p*-Me), 2.44 (s, 6H; *o*-Me), 3.40 (br, 1H; NH^9), 4.05 (br, 1H; NH^8), 4.14 (t, J(H,H) = 12.8 Hz, 1H; CH_2P), 4.49 (dd, J(P,H) = 10.2 Hz, J(H,H) = 13.2 Hz, 1H; CH_2P), 5.03 (q, J(H,H) = 5.6 Hz, 1H; H^7), 6.78 (dd, J(P,H) = 5.0, J(H,H) = 8.8 Hz, 1H; H^1), 6.88 (s, 1H; [C_6H_2]), 6.89 (s, 1H; [C_6H_2]), 7.39–7.0 (m, 11H; aromatic), 7.65–7.52 (m, 4H; aromatic).

The second diastereomer eluted was (R_C,R_P)-**5** (32 mg, 32%, >95% *de*. $[\alpha]_D^{20} = +133.8$ ($c = 1$); ^{31}P{^{1}H} NMR (101.26 MHz, $CDCl_3$): $\delta = 15.4$ (s); ^{1}H NMR (500 MHz, $CDCl_3$): $\delta = 1.78$ (d, J(H,H) = 6.5 Hz, 3H; Me), 2.02 (s, 6H; *o*-Me), 2.24 (s, 3H; *p*-Me), 3.45 (br, 1H; NH^9), 3.74 (t, J(H,H) = 13 Hz, 1H; PCH_2), 3.96 (br, 1H; NH^8), 4.85 (dd, J(H,H) = 13, J(P,H) = 9.5 Hz, 1H; PCH_2), 5.11 (m, J(H,H) = 5.5 Hz, 1H; H^7), 6.68 (s, 1H; [C_6H_2]), 6.69 (s, 1H; [C_6H_2]), 6.99 (dd, J(H,H) = 8.5, J(P,H) = 5.0 Hz, 1H; H^1), 7.18–7.16 (m, 2H; aromatic), 7.1–7.04 (m, 4H; aromatic), 7.36–7.26 (m, 5H; aromatic), 7.56 (d, J(H,H) = 8.5 Hz, 1H; H^6), 7.61 (d, J(H,H) = 8.0 Hz, 1H; H^3), 7.88 (m, 2H; *o*-C_6H_5P).

Synthesis of [PdCl(*R*-(+)-$C_{10}H_6CH(Me)NMe_2$){(±)-PBnMesPh}] (6): A suspension formed by **4** (170 mg, 0.25 mmol), PBnMesPh (160 mg, 0.50 mmol), and tetrahydrofuran (30 mL) was stirred at room temperature for 30 min and the resulting solution concentrated in vacuo. The solid obtained was recrystallized from acetone. Compound **6** (1:1 mixture of diastereomers) was isolated as a yellow solid (300 mg, 90%). ^{31}P{^{1}H} NMR (101.26 MHz, $CDCl_3$): $\delta = 11.7$ (s), 15.4 (s); MS (positive FAB): *m*/*z*: 622 $[M-Cl]^+$; elemental analysis calcd (%) for $C_{36}H_{39}ClNPPd$: C 65.66, H 5.97, N 2.13; found C 65.4, H 6.0, N 1.9.

Separation of diastereomers 6: Compound **6** (200 mg) was carefully eluted at room temperature, in a silica gel column (50 g silica gel) with $CHCl_3$/acetone (100:2) as eluent. The fractions eluted (15 mL) were concentrated in vacuo and checked by ^{1}H NMR spectroscopy. The fractions of the optically pure compound (by 200 MHz ^{1}H NMR spectroscopy) were selected using the aromatic proton signals H^1.The first diastereomer eluted was (R_C,S_P)-**6** (86 mg, 86%, >95% *de*). $[\alpha]_D^{20} = -75.84°$ ($c = 1$); ^{31}P{^{1}H} NMR (101.26 MHz, $CDCl_3$): $\delta = 14.3$ (s); ^{1}H NMR (500 MHz, $CDCl_3$): $\delta =$ 1.61 (d, J(H,H) = 6.5 Hz, 3H; MeCH), 2.31 (s, 3H; Me), 2.60 (d, 3H, J(H,P) = 1.5 Hz; Me^8), 2.64 (s, 6H; Me), 2.90 (d, J(H,P) = 3.0 Hz, 3H; Me^9), 4.11–4.05 (m, 2H; H^7, CH_2P), 4.36 (t, J(H,H) = J(H,P) = 12.5 Hz, 1H; CH_2P), 6.61 (dd, J(H,H) = 8.5 Hz, J(H,P) = 6.0 Hz, 1H; H^1), 6.94 (m, 3H; H^2, aromatic), 7.05–7.15 (m, 5H; aromatic), 7.18 (t, J(H,H) = 7.5 Hz, 1H; aromatic), 7.25–7.35 (m, 5H; *o*-$C_6H_5CH_2$, aromatic), 7.60–7.65 (m, 3H; H^6, aromatic).

The second diastereomer eluted was(R_C,R_P)-**6** (40 mg, 40%, >95% *de*. $[\alpha]_D^{20} = +9.87°$ ($c = 1$); ^{31}P{^{1}H} NMR (101.26 MHz, $CDCl_3$): $\delta = 19.0$ (s); ^{1}H NMR (500 MHz, $CDCl_3$): $\delta = 1.75$ (d, J(H,H) = 6.0 Hz, 3H; MeCH), 2.07 (s, 6H; Me), 2.21 (s, 3H; Me), 2.57 (d, J(H,P) = 1.5 Hz, 3H; Me^8), 2.87 (d, J(H,P) = 3.5 Hz, 3H; Me^9), 3.83 (t, J(H,H) = J(H,P) = 13.5 Hz, 1H; CH_2P), 4.21 (q, J(H,H) = J(H,P) = 6 Hz, 1H; H^7), 4.89 (dd, J(H,H) = 13.5 Hz, J(H,P) = 10.5 Hz, 1H; CH_2P), 6.65 (s, 1H; [C_6H_2]), 6.66 (s, 1H; [C_6H_2]), 6.88 (dd, J(H,H) = 8.5 Hz, J(H,P) = 5.5 Hz, 1H; H^1), 6.97 (d, J(H,H) = 8.5 Hz, 1H; H^2), 7.03–7.09 (m, 2H; aromatic), 7.24–7.38 (m, 7H;

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o-$C_6H_5CH_2$, aromatic), 7.60–7.65 (m, 3H; H^6, aromatic), 7.90–7.97 (m, 2H; *o*-C_6H_5P).

[Pd(μ-Cl){(2-CH_2-4,6-$Me_2C_6H_2$)PBnPh}]$_2$ (7): Compound **7** can be obtained, in the first fractions, when **5** or **6** were carefully eluted at room temperature, in a silica gel column with $CHCl_3$/acetone 100:5 or 100:2, respectively. Compound **7** can also be obtained if a suspension formed by **5** or **6** (0.25 mmol) and silica gel (3 g) in $CHCl_3$ was stirred at room temperature for 5 days. The resulting suspension was filtered and the silica gel was extracted with $CHCl_3$ to obtain **7** as a 2:1 mixture of diastereomers (70 mg, 60%). Elemental analysis calcd (%) for $C_{44}H_{44}Cl_2P_2Pd_2$: C 57.54, H 4.84; found C 57.6, H 5.0.

Major isomer: $^{31}P\{^1H\}$ NMR (101.26 MHz, $CDCl_3$): $\delta = 57.3$; ^1H NMR (250 MHz, $CDCl_3$, 240 K): $\delta = 2.14$ (s, 6H; Me), 2.25 (s, 6H; Me), 3.05 (br, 2H; CH_2Pd), 3.45 (br, 2H; CH_2Pd), 3.65 (br t, $J(H,H) = J(H,P) = 15$ Hz, 2H; CH_2P), 4.55 (br, 2H; CH_2P), 6.74 (s, 2H; [C_6H_2]), 6.98 (s, 2H; [C_6H_2]), 7.00–7.70 (br m, 20H; aromatic).

Minor isomer: $^{31}P\{^1H\}$ NMR (101.26 MHz, $CDCl_3$): $\delta = 57.9$; ^1H NMR (250 MHz, $CDCl_3$, 240 K): $\delta = 2.16$ (s, 6H; Me), 2.23 (s, 6H; Me), 3.05 (br, 2H; CH_2Pd), 3.45 (br, 2H; CH_2Pd), 3.65 (br t, $J(H,H) = J(H,P) = 15$ Hz, 2H; CH_2P), 4.55 (br, 2H; CH_2P), 6.79 (s, 2H; [C_6H_2]), 6.95 (s, 2H; [C_6H_2]), 7.00–7.70 (br m, 20H; aromatic).

The mononuclear complexes **8**, **9**, and **10** were obtained in an NMR tube by mixing **7** (20 mg) with a few drops of [D_5]pyridine or with the stoichiometric amount of triphenylphosphine or benzylmesitylphenylphosphine, respectively.

Compound 8: ^1H NMR (250 MHz, $CDCl_3$, 240 K): $\delta = 2.01$ (s, 6H; Me), 2.70 (br d, 1H; CH_2Pd), 2.99 (br d, 1H; CH_2Pd), 3.51 (t, $J(H,H) = J(H,P) = 15$ Hz, 1H; CH_2P), 4.52 (br, 1H; CH_2P), 6.64 (s, 1H; [C_6H_2]), 6.71 (s, 1H; [C_6H_2]), 7.03–7.60 (m, 10H; aromatic); $^{31}P\{^1H\}$ NMR (101.26 MHz, $CDCl_3$, 298 K): $\delta = 55.77$ (br s).

Compound 9: ^1H NMR (250 MHz, $CDCl_3$, 240 K): $\delta = 2.20$ (s, 3H; Me), 2.22 (s, 3H; Me), 2.20–2.48 (m, 2H; CH_2Pd), 3.77 (m, 1H; CH_2P), 4.67 (t, $J(H,H) = J(H,P) = 12.5$ Hz, 1H; CH_2P), 6.45 (s, 1H; [C_6H_2]), 6.81 (s, 1H; [C_6H_2]), 7.18–7.75 (m, 25H; aromatic); $^{31}P\{^1H\}$ NMR (101.26 MHz, $CDCl_3$, 240 K): $\delta = 51.50$ (d, $J(P,P) = 394$ Hz; P^1), 22.40 (d, $J(P,P) = 394$ Hz; P^2).

Compound 10 (1:1 mixture of diastereomers): ^1H NMR (250 MHz, $CDCl_3$, 240 K): $\delta = 1.95–2.37$ (m, 15H; Me), 3.53–3.63 (m, 2H; CH_2Pd), 3.92–5.02 (m, 4H; CH_2P), 6.55–7.56 (m, 24H; aromatic); $^{31}P\{^1H\}$ NMR (101.26 MHz, $CDCl_3$, 240 K): $\delta = 53.57$ (d, $J(P,P) = 396$ Hz; P^1), 50.96 (d, $J(P,P) = 397$ Hz; P^1), 6.31 (d, $J(P,P) = 396$ Hz; P^2), 4.91 (d, $J(P,P) = 397$ Hz; P^2).

Synthesis of [$PdCl_2${(±)-PBnMesPh}$_2$] (11): Benzylmesitylphenylphosphine (0.468 g, 1.47 mmol) was added to a solution of [$PdCl_2(PhCN)_2$] (0.289 g, 0.735 mmol) in tetrahydrofuran (25 mL) and stirred for 30 min at room temperature; the solution was then concentrated to dryness. The solid obtained was eluted by silica gel column chromatography with $CHCl_3$ as eluent. Compound **11** (1:1 mixture of diastereomers) was isolated as a yellow solid (150 mg, 25%). $^{31}P\{^1H\}$ (101.26 MHz, $CDCl_3$): $\delta = 7.99$ (s), 5.77(s); ^1H NMR (200 MHz, $CDCl_3$): $\delta = 1.97$ (s, 12H; o-Me), 2.12 (s, 12H; *o*-Me), 2.23 (s, 12H; *p*-Me), 3.75 (m, 4H; CH_2P), 4.25 (m, 4H; CH_2P), 6.72 (br s, 4H; Mes), 7.05–7.70 (m, 44H; aromatic); MS (positive FAB): *m*/*z*: 777 $[M-Cl]^+$, 742 $[M-2Cl]^+$; elemental analysis calcd (%) for $C_{44}H_{46}Cl_2P_2Pd$: C 64.92, H 5.70; found C 64.9, H 5.7.

Synthesis of ($R_P R_P$)- or ($S_P S_P$)-[$PdCl_2$(PBnMesPh)$_2$] (11): 1,2-Bis-(diphenylphosphino)ethane (0.236 g, 0.60 mmol) was added to a solution of optically pure **5** or **6** (0.60 mmol) in $CHCl_3$ (30 mL) and the mixture stirred under nitrogen for 15 min at room temperature. [$PdCl_2(PhCN)_2$] (0.116 g, 0.30 mmol) was added to the resulting suspension and the mixture stirred for 30 min at room temperature and then concentrated in vacuo. The solid obtained was eluted by silica gel column chromatography with $CHCl_3$ as eluent. Compound **12**, containing optically pure phosphine, was isolated as a yellow solid (60 mg, 25%). $^{31}P\{^1H\}$ (101.26 MHz, $CDCl_3$): $\delta = 7.99$; ^1H NMR (200 MHz, $CDCl_3$): $\delta = 2.12$ (s, 12H; *o*-Me), 2.23 (s, 6H; *p*-Me), 3.95 (dt, $J = 33.5$ Hz, $J = 13.1$ Hz, 2H; CH_2P), 4.25 (dt, $J = 33.21$, $J = 13.3$ Hz; 2H; CH_2P), 6.72 (s, 2H; Mes), 7.05–7.70 (m, 22H; aromatic).

Synthesis of [Pd(η^3-2-MeC_3H_4)Cl((±)-PBnMesPh)] (12): Benzylmesitylphenylphosphine (0.234 g, 0.735 mmol) was added to a solution of [Pd(μ-Cl)(η^3-2-MeC_3H_4)]$_2$ (0.145 g, 0.367 mmol) in tetrahydrofuran (25 mL) and the mixture stirred for 30 min at room temperature, then tetrahydrofuran was replaced by diethyl ether and [Pd(η^3-2-MeC_3H_4)Cl((±)-PBnMesPh)] precipitates as a white solid as a 1:1 mixture of diastereomers. The solid obtained was eluted by silica gel column chromatography with $CHCl_3$/acetone (100:4) as eluent. Compound **12** was isolated as a yellow solid (0.265 g, 70%). $^{31}P\{^1H\}$ NMR (101.26 MHz, $CDCl_3$): $\delta = 17.5$ (s), 17.8 (s); ^1H NMR (500 MHz, $CDCl_3$): $\delta = 1.60$ (s, 3H; Me), 1.88 (s, 3H; Me), 2.17 (s, 6H; *o*-Me), 2.25 (s, 3H; *p*-Me), 2.26 (s, 3H; *p*-Me), 2.27 (s, 1H; H^d), 2.29 (s, 6H; *o*-Me), 2.51 (s, 1H; H^d), 3.12 (br, 1H; H^c), 3.26 (d, $J = 2.5$ Hz, 1H; H^c), 3.33 (d, $J = 9.5$ Hz, 1H; H^b), 3.34 (d, $J = 10.5$ Hz, 1H; H^b), 4.05–4.25 (m, 4H; CH_2), 4.32 (dd, $J = 7.75$, $J = 3.0$ Hz, 1H; H^a), 4.36 (dd, $J = 6.5$, $J = 3.0$ Hz, 1H; H^a), 6.78 (d, $J = 3.0$ Hz, 2H; Mes), 6.82 (d, $J = 2.5$ Hz, 2H; Mes), 7.00–7.30 (m, 20H; aromatic); elemental analysis calcd (%) for $C_{26}H_{30}ClPPd$: C 60.60, H 5.87; found C 60.3, H 5.8. Crystals of **12** for X-ray structure determination were obtained from diethyl ether.

Synthesis of [Pd(η^3-2-MeC_3H_4)Cl{(R_P)-PBnMesPh}] or [Pd(η^3-2-MeC_3H_4)Cl{(S_P)-PBnMesPh}] (12): 1,2-Bis-(diphenylphosphino)ethane (0.059 g, 0.15 mmol) was added to a solution of optically pure **5** or **6** (0.15 mmol) in $CHCl_3$ (30 mL) and the mixture stirred under nitrogen for 15 min at room temperature. [Pd(μ-Cl)(η^3-2-MeC_3H_4)]$_2$ (0.029 g, 0.075 mmol) was added to the resulting suspension and the mixture stirred for 30 min at room temperature, then concentrated in vacuo. The solid obtained was eluted by silica gel column chromatography with $CHCl_3$/acetone (100:4) as eluent. Compound (R_P)- or (S_P)-**12** was isolated as a yellow solid (0.055 g, 70%). Crystals of [Pd(η^3-2-MeC_3H_4)Cl{(S_P)-PBnMesPh}] for X-ray structure determination were obtained from diethyl ether.

Hydrovinylation reaction: Hydrovinylation reactions were performed in a stainless-steel autoclave fitted with an external jacket connected to an isobutanol bath and the temperature controlled using a thermostat to ±0.5 °C. The internal temperature was monitored by means of a thermocouple. Internal temperature and pressure as a function of time were registered with a Linseis L-200 Recorder.

A mixture of 4.0×10^{-5} mol of the neutral palladium complex, 4.4×10^{-5} mol $AgBF_4$ and styrene (0.0400 mol) in freshly distilled CH_2Cl_2 (10 mL) was stirred for 5 min in the dark in a nitrogen atmosphere. After filtering off the AgCl formed, the solution was placed in a thermostat-fitted autoclave, which had previously been purged with successive applications of vacuum and argon, and ethylene was admitted until a pressure of 15 bar was reached. After the desired time the autoclave was slowly depressurized, 10% HCl (10 mL) added, and the mixture stirred for 10 min in order to quench the catalyst. The CH_2Cl_2 layer was decanted and dried with Na_2SO_4. The quantitative distribution of product fractions was determined by GC analysis.

Crystallographic studies: A prismatic crystal of racemic-**12** ($0.1 \times 0.1 \times 0.1$ mm) or (S_P)-**12** ($0.1 \times 0.1 \times 0.2$ mm) was selected and mounted on an Enraf-Nonius CAD4 diffractometer. Unit-cell parameters were determined from automatic centering of 25 reflections ($12 < \theta < 21°$) and refined by least-squares method. Intensities were collected with graphite-monochromatized $Mo_{K\alpha}$ radiation, using $\omega/2\theta$ scan technique. For racemic-**12**, 7127 reflections were measured in the range $2.16 \le \theta \le 29.96$, 7083 of which were nonequivalent by symmetry (R_{int} (on I) = 0.039). 2029 Reflections were assumed as observed applying the condition $I > 2\sigma(I)$. For (S_P)-**12**, 3846 reflections were measured in the range $2.20 \le \theta \le 29.96$, 3639 of which were nonequivalent by symmetry (R_{int} (on I) = 0.035). 1898 Reflections were assumed as observed applying the condition $I > 2\sigma(I)$. For both crystals three reflections were measured every two hours as orientation and intensity control, significant intensity decay was not observed. Lorentz-polarization but not absorption corrections were made. A summary of experimental details is given in Table 4.

The structures were solved by direct methods, using the SHELXS computer program and refined by a full-matrix least-squares method, with the SHELX97 program,[37] using 7083 reflections for racemic-**12** and 3639 reflections for (S_P)-**12** (very negative intensities were not assumed). The function minimized was $\Sigma\, w[|F_o|^2 - |F_c|^2]^2$, where $w = [\sigma^2(I) + (0.0831\,P)^2]^{-1}$ for racemic-**12** and $w = [\sigma^2(I) + (0.0404\,P)^2]^{-1}$ for (S_P)-**12**, being $P = (|F_o|^2 + 2|F_c|^2)/3$; f, f' and f'' were taken from the International Tables of X-Ray Crystallography.[38] The chirality of (S_P)-**12** was defined from the Flack coefficient, which is equal to 0.04(6) for the given results.[39] For racemic-**12** the final R (on F) factor was 0.041, wR (on F^2) = 0.113 and the goodness of fit 0.801 for all observed reflections. The number of refined

Table 4. Crystal data and structure refinement for **12**.

	rac-**12**	(S_P)-**12**
formula	$C_{26}H_{31}ClPPd$	$C_{26}H_{31}ClPPd$
F_W	515.32	515.32
T [K]	293(2)	293(2)
λ [Å]	0.71069	0.71069
crystal system	triclinic	monoclinic
space group	$P\bar{1}$	$P2_1$
a [Å]	8.117(4)	9.403(2)
b [Å]	11.806(2)	13.763(3)
c [Å]	13.604(3)	9.587(4)
α [°]	77.94(2)	
β [°]	83.29(3)	100.16(2)
γ [°]	73.28(2)	
V [Å^3]	1218.7(7)	1221.2(6)
Z	2	2
ρ_{calcd} [Mg m^3]	1.407	1.401
μ [mm^{-1}]	0.946	0.944
$F(000)$	530	528
crystal size [mm]	$0.1 \times 0.1 \times 0.2$	$0.1 \times 0.1 \times 0.2$
θ range [°]	2.16 to 29.96	2.20 to 29.96
reflections collected	7127	3846
reflections unique	7083	3639
data/restraints/parameters	7083/12/262	3639/1/278
GoF on F^2	0.800	0.978
final R indices [$I > 2\sigma(I)$]	$R1 = 0.0419$	$R1 = 0.0625$
	$wR2 = 0.1133$	$wR2 = 0.0993$
R indices (all data)	$R1 = 0.2054$	$R1 = 0.1944$
	$wR2 = 0.1838$	$wR2 = 0.1257$
largest diff. peak/hole [e Å^{-3}]	0.905/ − 0.615	0.895/ − 0.743

parameters was 262. Max. shift/esd = 0.00, mean shift/esd = 0.00. Max. and Min. peaks in final difference synthesis were 0.905 and −0.615 e Å^{-3}, respectively. For (S_P)-**12** the final R (on F) factor was 0.062, wR (on F^2) = 0.099 and the goodness of fit 0.977 for all observed reflections. The number of refined parameters was 278. Max. shift/esd = 0.00, mean shift/esd = 0.00. Max. and Min. peaks in final difference synthesis were 0.895 and −0.743 e Å^{-3}, respectively.

CCDC-172978 and 172979 contain the supplementary crystallographic data for this paper. These data can be obtained free of charge via www.ccdc.cam.ac.uk/conts/retrieving.html (or from the Cambridge Crystallographic Data Centre, 12 Union Road, Cambridge CB2 1EZ, UK; (fax: (+44) 1223-336-033; or e-mail: deposit@ccdc.cam.ac.uk).

Computational details: All the calculations were performed with the Spartan 5.1 suite of programs.[40] The molecular mechanics geometry optimizations were done using the MMFF94 force field[41] with the parameters supplied by the program.

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