Resolution of Benzylcyclohexylphenylphosphine by Palladium(II)−Amine Metallacycles. A New Ligand for Asymmetric Hydrovinylation

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The synthesis of benzylcyclohexylphenylphosphine and its resolution by means of optically active palladium metallacycles are reported. The absolute configuration of (R_C,S_P)-[PdCl(C_6H_4-CHMeNMe$_2$)(PBzCyPh)] has been determined by single-crystal X-ray analyses. The allyl complex [Pd(η^3-2-MeC_3H_4)(PBzCyPh)S]BF_4, prepared in situ from [Pd(η^3-2-MeC_3H_4)Cl-(PBzCyPh)] and $AgBF_4$ in CH_2Cl_2 solution, was used as a precatalyst for asymmetric hydrovinylation of styrene and 2-vinylnaphthalene. This system permits the synthesis of 3-phenyl-1-butene and 3-(2-naphthyl)-1-butene with good *ee* values working in very mild conditions of temperature (15 °C).

Introduction

Spectacular progress has been made in the field of asymmetric catalysis by using homogeneous catalysts based on transition metal complexes modified by chiral ligands. In this way chiral phosphines have become very important in asymmetric catalysis.[1] Among the plenitude of chiral phosphines developed for application in asymmetric catalysis, examples of monodentate ligands possessing a stereogenic phosphorus atom are rare, even though metal complexes featuring marked asymmetry near the catalytic center are considered to be excellent optical inducers.[2] In some catalytic processes such as the hydrovinylation reaction the catalyst becomes inactive in the presence of bidentate phosphines and particular attention has thus been given to systems containing Horner phosphines. Unfortunately optically pure Horner phosphines are not easy to prepare, and a series of phosphines having optically active substituents such as menthyl or myrtanyl have been synthesized and used in asymmetric hydrovinylation as an alternative.[1e,3]

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, which are widely used as antiinflammatory drugs, such as ibuprofen and naproxen.[4] [MCl(allyl)L] compounds (M = Ni, Pd; L = monodentate phosphine) are precursors of active species in the catalytic hydrovinylation of olefins, and the activity of the catalyst increases with increasing bulk of the modifying ligand, up to a certain point, beyond which a sharp decline is observed.[3a] These facts prompted us to prepare the benzylcyclohexylphenylphosphine, which due to its steric bulk and electronic features, seems to be a promising precursor of active species in the asymmetric hydrovinylation of olefins.

We report the synthesis of this monodentate phosphine, its resolution by palladium metallacycles, the synthesis of the optically active allyl compound [Pd(η^3-2-MeC_3H_4)Cl(PBzCyPh)], and studies of the asymmetric hydrovinylation of styrene and 2-vinylnaphthalene, using this allyl complex as a precursor of catalytic species.

Discussion and Results

The chiral phosphine was synthesized by reaction between dibenzylphenylphosphine and lithium metal in THF under a dry nitrogen atmosphere. After 20 h of stirring at room temperature complete cleavage of one of the CH_2−P bonds of the dibenzylphenylphosphine was accomplished, with the formation of the phenylbenzylphosphide anion. ^{31}P NMR spectra, under nitrogen, clearly illustrated the formation of this anion (δ = −37.1 ppm) and were used to monitor the progress of the reaction. Subsequent addition of cyclohexyl bromide afforded the racemic (±)-benzylcyclohexylphenylphos-

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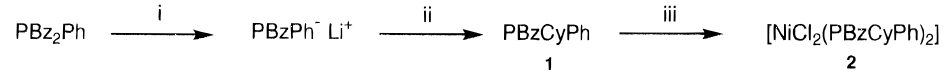
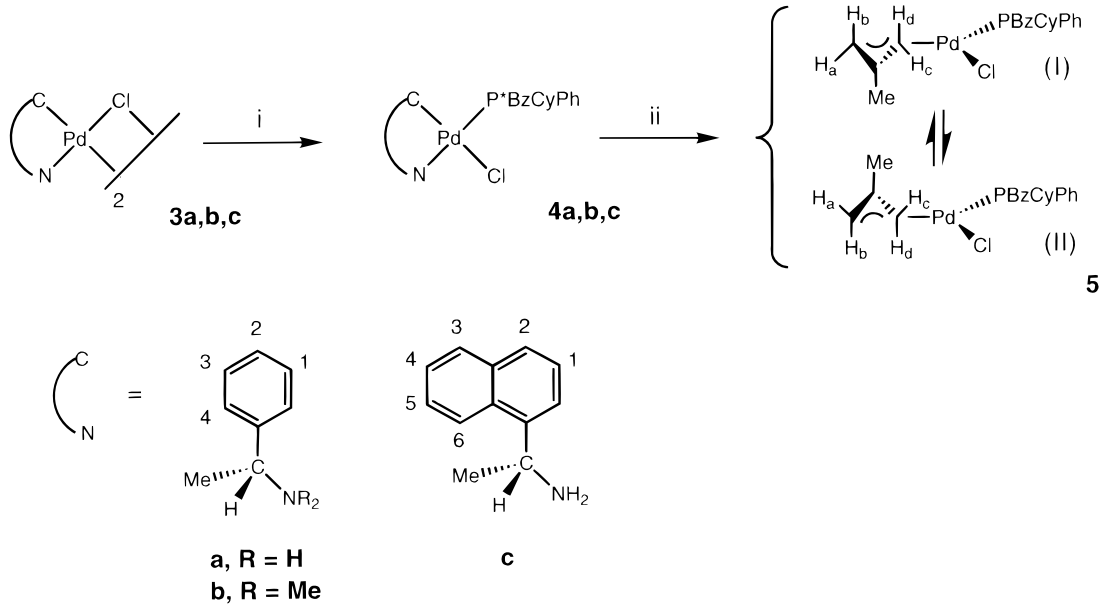
Scheme 1[a]



[a] (i) Li, THF, room temperature, 20 h; (ii) $C_6H_{11}Br$, THF, room temperature, 10 min; (iii), $NiCl_2$, THF/EtOH, room temperature, 15 min.

Scheme 2[a]



[a] (i) $[NiCl_2(PBzCyPh)_2]$, THF, room temperature, 45 min; (ii) dppe, $[Pd(\mu\text{-Cl})(\eta^3\text{-2-Me}C_3H_4)]_2$, ether, room temperature, 45 min.

phine **1**, in THF solution. A saturated solution of $NiCl_2$ in absolute ethanol was added to the organic layer, and then the resulting solution was stirred for 15 min and concentrated in vacuo to afford dark red crystals of the complex dichlorobis[(±)-benzylcyclohexylphenylphosphine]nickel(II) (**2**) (see Scheme 1).

Benzylcyclohexylphenylphosphine is readily oxidable and should be stored under nitrogen, but when coordinated to nickel, this ligand becomes very stable and can be stored for several months in air. Besides, this nickel coordination compound permits the synthesis of metallacycles **4**, by ligand transfer reactions (see Scheme 2).

The versatility of ortho-palladated derivatives of optically active N-donor ligands as resolving agents for Lewis bases has been convincingly demonstrated. These complexes have been widely used for the resolution of bidentate and monodentate ligands.[5] The optically pure cyclopalladated dinuclear compounds **3** were obtained from the optically active amines as reported.[6] Reaction of dimers **3** with the coordination compound dichlorobis-[(±)-benzylcyclohexylphenylphosphine]nickel(II) afforded the mononuclear complexes [PdCl(C−N)(PBzCyPh)], as a 1:1 mixture of diastereoisomers (R_C,R_P)-**4** and (R_C,-S_P)-**4** (see 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, 2D-NMR experiments and positive FAB-mass spectra were carried out to complete the characterization. The high-field shift of the aromatic protons of the palladated ring in **4**, due to the aromatic rings of the phosphine, indicates the cis disposition of the phosphorus relative to the metalated carbon atom, and the chemical shift of the phosphorus in **4** confirms this arrangement.[7]

Resolution of the Phosphine. Attempts to separate the diastereoisomers (R_C,R_P)-**4a** and (R_C,S_P)-**4a** by recrystallization were unsuccessful, but the elution of the mixture of (R_C,R_P)-**4a** and (R_C,S_P)-**4a** through a SiO_2 column, using chloroform−acetone (100:2) as eluent, allowed the separation of the diastereoisomer (R_C,R_P)-**4a** in 84% yield (42% with respect to the total Pd), with a 90% de (see below for the assignment of absolute configuration). Nevertheless, better results were obtained with **4b** and **4c**. The recrystallization of a saturated solution of a mixture of (R_C,R_P)-**4b** and (R_C,S_P)-**4b** in ether afforded the diastereoisomer (R_C,S_P)-

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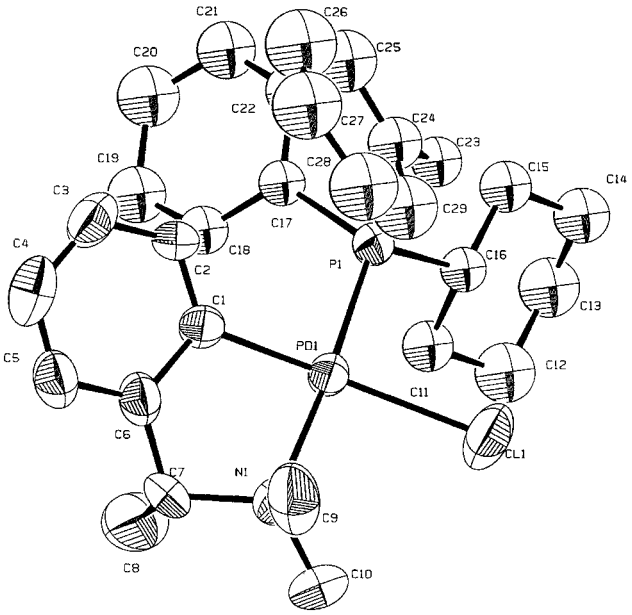

Figure 1. ORTEP plot of the structure of (R_C,S_P)-**4b**.

Table 1. Selected Bond Lenghts (Å) and Angles (deg) for (R_C,S_P)-4b

Pd(1)−Cl(1)	2.418(4)	Cl(1)−Pd(1)−P(1)	92.2(1)
Pd(1)−P(1)	2.244(3)	Cl(1)−Pd(1)−N(1)	90.9(3)
Pd(1)−N(1)	2.13(1)	P(1)−Pd(1)−C(1)	96.2(3)
Pd(1)−C(1)	2.00(1)	N(1)−Pd(1)−C(1)	82.1(4)
P(1)−C(11)	1.86(1)	C(11)−P(1)−C(17)	102.8(5)
P(1)−C(17)	1.81(1)	C(11)−P(1)−C(23)	101.6(5)
P(1)−C(23)	1.82(1)	C(17)−P(1)−C(23)	108.9(6)
N(1)−C(7)	1.54(2)		
N(1)−C(9)	1.46(2)		
N(1)−C(10)	1.47(2)		
C(1)−C(2)	1.33(1)		
C(1)−C(6)	1.41(1)		

4b in 70% yield (35% with respect to the total Pd) with a de higher than 95%, and the elution of the mixture of (R_C,R_P)-**4c** and (R_C,S_P)-**4c** in a SiO_2 column (30 × 400 mm, 50 g SiO_2) with $CHCl_3$−acetone (100:3) as eluent permitted the separation of the diastereoisomers (R_C,R_P)-**4c** and (R_C,S_P)-**4c** in 70 and 66% yield, respectively (35 and 33% with respect to the total Pd), with a de higher than 95% in both cases.

The absolute configuration of the phosphine in (R_C,S_P)-**4b** was determined by X-ray crystallography (Figure 1). The crystal structure consists of discrete molecules separated by van der Waals distances. Bond distances and angles are similar to those reported for related metallacycles; see Table 1.[7b,c] The palladium atom is in a square-planar environment, coordinated to carbon, chlorine, nitrogen, and phosphorus atoms. The coordination plane shows a tetrahedral distortion, the deviation from the mean plane being +0.08, +0.43, −0.01, and −0.18 Å for Cl, C1, P, and N, respectively. The phosphorus and nitrogen atoms adopt a trans arrangement, and the absolute configuration of the phosphine ligand in this diastereoisomer is *S*.

The action of 1,2-bis(diphenylphosphino)ethane (dppe) on the optically pure cyclopalladated derivatives **4** led to the enantiopure free phosphine PBzCyPh (^{31}P NMR: $\delta = -6.1$). The displacement proceeds with retention of the configuration at phosphorus, as verified by the quantitative regeneration of the starting material **4** from the free ligand and the corresponding dinuclear cyclopalladated derivative **3**. The free phosphine is readily oxidable and should be stored under nitrogen, but no racemization was observed when the phosphine was stored for several days in THF solution. The addition of dppe to solutions of each one of the different diastereoisomers of **4a** or **4c** and subsequent reaction of the free phosphine formed with the cyclopalladated compound **3b** permitted the determination of the absolute configuration of the phosphine on each of the diastereoisomers by ^{31}P NMR.

Synthesis of [Pd(η^3-2-MeC_3H_4)Cl(PBzCyPh)], 5. This compound, containing the racemic phosphine as ligand, was obtained by reaction between dichlorobis-[(±)-benzylcyclohexylphenylphosphine]nickel(II) and the dinuclear allyl complex [Pd(μ-Cl)(η^3-2-MeC_3H_4)]$_2$, in toluene. This complex was characterized by elemental analysis, IR spectra, FAB-mass spectra, and ^{1}H and ^{31}P NMR spectra. NMR data show that **5** occurs in two diastereomeric forms, I and II, because of the lack of a symmetry plane in this complex (see Scheme 2). Proton NMR data of the allylic group were assigned by comparison with literature values.[8] Unusually high-field shifts of H^c and H^d were observed, showing that these protons are in close proximity to aromatic phosphine rings. 2D ^{1}H NMR ROESY experiments, carried out in $CDCl_3$ solutions, permitted the unambiguous assignment of the NMR spectrum. In addition to the negative NOE cross-peaks which arise from cross-relaxation, the phase-sensitive 2D ROESY experiment also shows a series of positive cross-peaks connecting the diastereoisomers I and II of compound **5**, thereby indicating that these isomers are in equilibrium in solution; see Table 2. These data also show that the interconversion between both diastereoisomers mainly occurs via the $\pi-\sigma-\pi$ process, by opening the Pd−C bond trans to the phosphorus atom. The syn−syn, anti−anti exchange (apparent allyl rotation) is also observed.[8,9]

The X-ray structure of **5**, containing racemic phosphine as ligand, has been determined (Figure 2). Compound **5** crystallizes in the $P2_1/n$ group. The crystal structure consists of discrete molecules separated by van der Waals distances. The unit cell contains only the stereoisomers S_P-I and R_P-II, these molecules being one of the two pairs of enantiomers possible. The structure confirms 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

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Table 2. Selected 2D ^{1}H NMR ROESY Data for 5[a]

negative NOEs	exchange cross-peaks (positive NOEs)
H^a(isomers I, II) [4.45]···H^b(isomer II) [3.44] (s)	H^a(isomers I, II) [4.45]···H^c(isomer I) [2.95] (m)
H^a(isomers I, II) [4.45]···H^b(isomer I) [3.41] (s)	H^a(isomers I, II) [4.45]···H^c(isomer II) [2.89] (m)
H^c(isomer I) [2.95]···H^d(isomer I) [2.03] (s)	H^b(isomer II) [3.44]···H^d(isomer I) [2.03] (m)
H^c(isomer II) [2.89]···H^d(isomer II) [2.44] (s)	H^b(isomer I) [3.41]···H^d(isomer II) [2.44] (m)
H^a(isomers I, II) [4.45]···Me (isomer I) [1.86] (w)	H^c(isomer I) [2.95]···H^d(isomer II) [2.44] (s)
H^a(isomers I, II) [4.45]···Me (isomer II) [1.76] (w)	H^c(isomer II) [2.89]···H^d(isomer I) [2.03] (s)
H^c(isomer I) [2.95]···Me (isomer I) [1.86] (w)	
H^c(isomer II) [2.89]···Me (isomer II) [1.76] (w)	

[a] In $CDCl_3$ at 20 °C; values in brackets are the proton chemical shifts in ppm; s = strong, m = medium, w = weak.

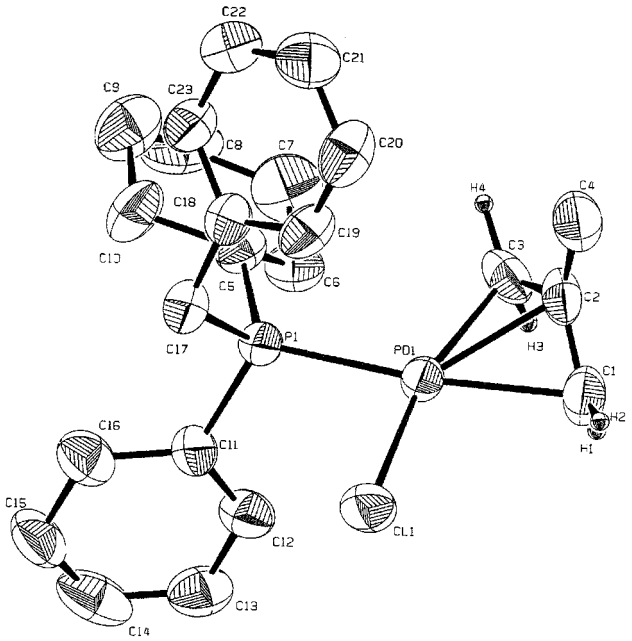

Figure 2. ORTEP plot of the structure of **5**.

Table 3. Selected Bond Lenghts (Å) and Angles (deg) for 5

Pd(1)−Cl(1)	2.356(2)	Cl(1)−Pd(1)−P(1)	92.04(8)
Pd(1)−P(1)	2.292(2)	Cl(1)−Pd(1)−C(1)	98.7(3)
Pd(1)−C(1)	2.178(9)	C(1)−C(2)−C(3)	113.7(9)
Pd(1)−C(2)	2.162(8)	C(1)−C(2)−C(4)	123.3(9)
Pd(1)−C(3)	2.104(9)		
P(1)−C(5)	1.811(9)		
P(1)−C(11)	1.838(9)		
P(1)−C(17)	1.830(9)		
C(1)−C(2)	1.38(1)		
C(2)−C(3)	1.44(1)		
C(2)−C(4)	1.48(1)		

with respect to the chloro ligand; see Table 3.[10] 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 68.7°. The methyl group is 0.2 Å out of the plane defined by C1, C2, and C3, the other carbon atoms of the allyl ligand.

Compound **5**, containing the phosphine in optically pure form, can be obtained by the addition of dppe to a solution of one of the optically pure diastereoisomers **4**, in a 1:1 ratio, and subsequent reaction of the free phosphine formed with the dinuclear allyl complex $[Pd(\mu\text{-}Cl)(\eta^3\text{-}2\text{-}MeC_3H_4)]_2$.

Catalytic Hydrovinylation. Palladium and nickel π-allyl compounds are good precursors for the catalytic hydrovinylation of olefins. Although important details remain unclear, it is generally accepted that the key intermediate is a cationic M(II) hydride complex (see Scheme 3), which reacts with the olefin to afford a metal−alkyl bond stabilized, in the case of vinylaromatic derivatives, in the form of an η^3-benzylic complex. This is the step where the asymmetric induction is created.[11] Insertion of the second olefin into the metal−carbon bond, followed by a β-elimination reaction, gives the organic product and regenerates the metal-hydride catalyst.[3,12,13]

The main interest in hydrovinylation reaction lies in the generation of a new asymmetric center, and considerable effort has been invested in obtaining high enantioselectivity by modifying the metal atom with optically active ligands. Highly enantioselective hydrovinylation of styrene to produce 3-phenyl-1-butene in 95% enantiomeric excess has been described using the allyl−nickel complex $[Ni(\eta^3\text{-}C_3H_5)ClL^*]$ in the presence of Et_2AlCl, where L* is a dimeric aminophosphine derived from (*R*)-myrtenal and (*S*)-1-phenylethylamine, but reaction temperatures as low as −70 °C are needed.[1e,3a] The same system has been used to obtain (−)-(*R*)-3-(6-methoxy-2-naphthyl)-1-butene, a naproxen intermediate, in 72% yield and 83.2% enantiomeric excess.[14] Recently, it has been shown that the hydrovinylation of various vinylarenes proceeds with an excellent chemical yield and selectivity, when a combination of allylnickel bromide dimer, a weakly coordinating counterion such as triflate, and a monophosphine is employed as the precatalyst. In addition, an enantioselectivity up to 80% was obtained when the reaction was performed at −70 °C, using an optically active monophosphine that carries a hemilabile group.[15] Palladium compounds $[Pd(\eta^3\text{-}C_3H_4R)L]X$ (L = menthyldialkyl- or alkylarylphosphinite, X = SbF_6, ClO_4, BF_4; CF_3SO_3) catalyze the asymmetric hydrovinylation of styrene at 0 °C to give 3-phenyl-1-butene in 34% yield with 80% enantiomeric excess.[16]

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Scheme 3

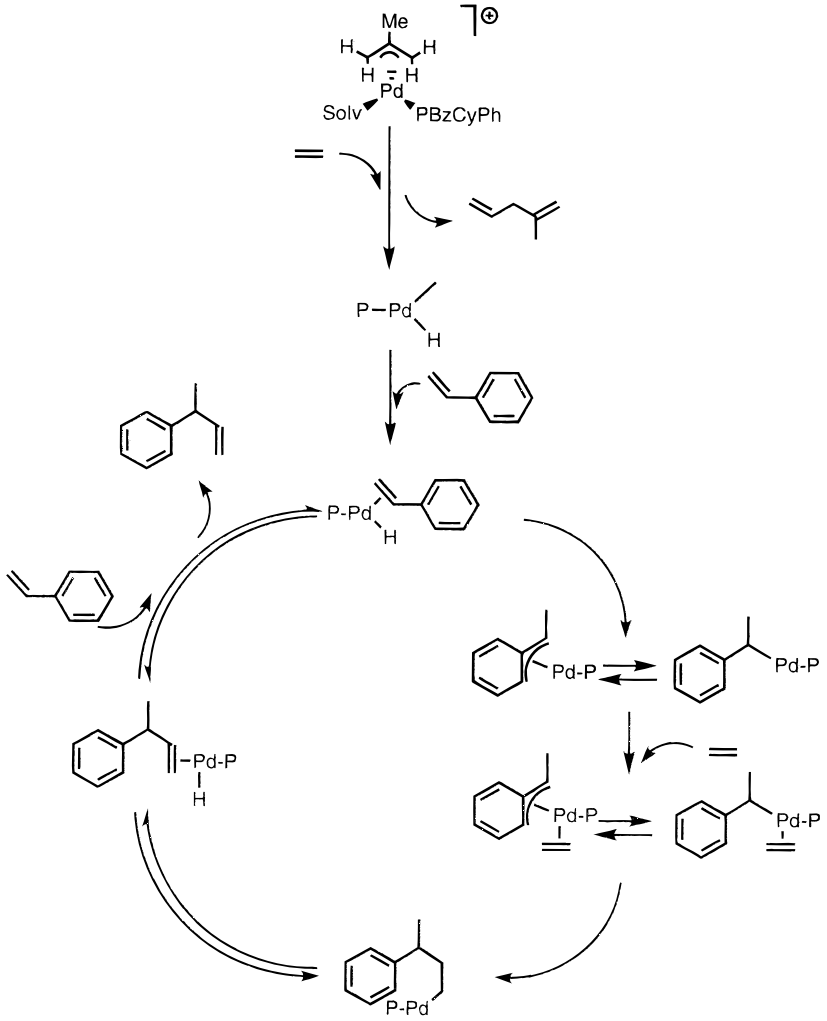

Table 4. Hydrovinylation Reaction of Styrene and 2-Vinylnaphthalene[a]

run	catalyst[b]	olefin	solvent	*T* (°C)	*t* (min)	conversion (%)[c]	selectivity (%)[d]	C16-fraction (%)[e]	TOF/h[f]	ee (%)
1	rac	styrene	THF	10	60	16.2	100	0.6	56	
2	*R*	styrene	THF	25	60	33.2	99	3.0	300	45-*S*
3	rac	styrene	CH_2Cl_2	0	120	13.2	100	0.8	62	
4	*R*	styrene	CH_2Cl_2	5	90	64.8	99	4.3	405	61-*S*
5	rac	styrene	CH_2Cl_2	10	60	61.5	97	3.2	585	
6	*R*	styrene	CH_2Cl_2	15	30	61.5	98	5.5	1290	60-*S*
7	*S*	styrene	CH_2Cl_2	15	30	32.5	99	2.9	590	59-*R*
8	rac	styrene	CH_2Cl_2	15	60	99.9	83	5.2	947	
9	*S*	2-vinylnaphthalene	CH_2Cl_2	15	20	83.0	98.5		250	84-*R*
10	*R*	2-vinylnaphthalene	CH_2Cl_2	15	60	100	58		100	85-*S*
11	**6**	styrene	CH_2Cl_2	15	30	21.3	100	1.2	400	

[a] Initial ethylene pressure 15 bar; ratio olefin/catalyst 1000:1 for styrene and 100:1 for 2-vinylnaphthalene. [b] Catalyst: filtered solutions of (R_P)-**5** or (S_P)-**5** + olefin + $AgBF_4$, except for run 11, where compound **6** was used. [c] Conversion of starting olefin. [d] Selectivity: % of 3-aryl-1-butene with respect to the hydrovinylation fraction (3-aryl-1-butene and 2-aryl-2-butenes). [e] C16-fraction: styrene dimers. [f] TOF/h calculated as the total amount of arylbutenes formed.

The complex [Pd(η^3-2-MeC_3H_4)(PBzCyPh)S]BF_4, prepared in situ from **5** and $AgBF_4$ in CH_2Cl_2 solution, was used as a catalyst for asymmetric hydrovinylation of styrene and 2-vinylnaphthalene, and the results are shown in Table 4. Optical rotation measurements show that (−)-(*R*)-3-phenyl-1-butene and (−)-(*R*)-3-(2-naphthyl)-1-butene were obtained from (S_P)-**5**. We should emphasize the great activity of this catalyst (up to 1290 cycles per palladium atom and hour), the excellent selectivity, the low amount of dimers formed (ranging between 0.6 and 5.5%), and the ee values obtained, 60% for 3-phenyl-1-butene and 85% for 2-(2-naphthyl)-1-butene. It should also be noted that these results were obtained in mild conditions of temperature (15 °C) and ethylene pressure (15 bar).[17,18]

As can be seen in runs 1 and 2, the solvent has an important role in the hydrovinylation reaction, influencing both activity and enantioselectivity. This suggests that solvent molecules could be coordinated to the metal atom in some steps of the catalytic cycle, stabilizing species with low coordination numbers. One such step

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is the coordination of the styrene derivative to the metal center, where the asymmetric induction is created. As expected, the reactions in THF are slower than those in dichloromethane, due to the higher donor properties of tetrahydrofuran, which can compete strongly with the olefins for the coordination to the palladium center.

We also tested a cationic complex as a catalyst precursor. For this purpose we had synthesized the complex **6,** $[Pd(\eta^3\text{-}2\text{-}MeC_3H_4)(NCCH_3)(PBzCyPh)]BF_4$. This catalyst (run 11) presented lower activity than the one generated in situ, probably due to the presence of acetonitrile, which can compete with alkenes for the coordination to the palladium atom.

The results obtained with this optically pure Horner phosphine are of the same order as those obtained with hemilabile *P*-chiral phosphines.[3a,16] Active species containing only one phosphine per metal atom and the proximity of the stereogenic center to the metal can explain this. The results of RajanBabu et al.[15] using an allyl−nickel system with functionalized phosphines with the stereogenic center in the labile arm of the phosphine may be related with the availability of the fifth coordination position in nickel complexes and its importance in the control of the selectivity of the reaction. In conclusion, phosphines such as benzylcyclohexylphenylphosphine are good ligands for asymmetric homogeneous catalysis, and experiments testing this type of phosphines in other catalytic reactions are currently in progress.

Experimental Section

Experimental Section. ^{1}H NMR at 200 MHz and $^{13}C\{^1H\}$ at 50.3 MHz were recorded on a Varian Gemini 200 spectrometer, and ^{1}H NMR at 500 MHz, ^{13}C NMR at 75.4 MHz, and $^{31}P\{^1H\}$ at 101.26 MHz were recorded, respectively, on a Varian VXR 500, a Varian 300, and a Bruker DRX 250 spectrometer. Chemical shifts (in ppm) were measured relative to $SiMe_4$ for ^{1}H and ^{13}C and to 85% H_3PO_4 for ^{31}P. The solvents used were $CDCl_3$ in ^{1}H and THF or $CHCl_3$ in ^{31}P. Microanalyses were performed at the Institut de Química Bio-Orgànica de Barcelona and the Serveis Científico-Tècnics de la Universitat de Barcelona. Infrared spectra were recorded as KBr disks on a Nicolet 520 FT-IR spectrometer. GC analyses were performed on a Hewlett-Packard 5890 series II chromatograph equipped with a 50 m ultra-2 cross-linked 5% phenylmethyl silicone capillary column and a FID detector connected to an HP 3396A integrator. Mass spectra were obtained with a Hewlett-Packard 5890 series II chromatograph with the same column coupled to a Hewlett-Packard 5971A mass selective detector. Enantiomeric excess was determined by GC analysis with a Hewlett-Packard 5890 chromatograph fitted with a 25 m FS-CYCLODEX column. Helium was used as carrier gas in all cases. The optical rotations of the complexes (c = g/100 mL, in $CHCl_3$) were determined 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-nitrobenzyl alcohol for FAB analysis and then subjected to bombardment with cesium atoms.

Materials and Synthesis. All the reactions involving free phosphines were carried out using Schlenk techniques under nitrogen atmosphere. All solvents were dried and degassed by standard methods. Tetrahydrofuran and toluene were distilled over sodium benzophenone, under nitrogen, before use. CH_2Cl_2 was distilled over CaO−$CaCl_2$. All chemical were of commercial grade and used as received, except for 2-vinylnaphthalene, which was recrystallized from ethanol−water in order to eliminate the small amount of 2-naphthaldehyde that it contains. Cyclopalladated compounds **3**, PBz_2Ph, and $[Pd(\mu\text{-}Cl)(\eta^3\text{-}2\text{-}MeC_3H_4)]_2$ were prepared according to procedures described elsewhere.[6,19,20]

Synthesis of (±)-Benzylcyclohexylphenylphosphine. Small pieces of lithium (0.086 g, 12.4 mmol) were added to a solution of dibenzylphenylphosphine (1.5 g, 5.17 mmol) in THF (40 mL), and the reaction mixture was stirred for 20 h at 20 °C. The excess of lithium was removed by decantation, cyclohexyl bromide (0.94 mL, 7.63 mmol) was added, and the mixture was stirred for 10 min. The resulting solution was washed twice in 10 mL of an aqueous solution of ammonium chloride (15%) and concentrated in vacuo to afford (±)-benzylcyclohexylphenylphosphine as an oil, which can be characterized by NMR spectroscopy. ^{31}P (101.26 MHz): δ = −6.13 s. ^{1}H NMR (250 MHz, $CDCl_3$): δ = 7.52−7.48 (m, 2H, aromatic), 7.20−7.05 (m, 8H, aromatic), 3.06 (dd, 1H, J = 24.0, J = 13.5, CH_2), 3.05 (dd, 1H, J = 24.0, J = 13.5, CH_2), 1.95−1.85 (m, 1H, aliphatic), 1.80−1.50 (m, 5H, aliphatic), 1.40−1.10 (m, 5H, aliphatic). ^{13}C NMR (75.4 MHz, $CDCl_3$): δ = 138.35 (d, J = 6.3 Hz, *Bz*), 136.22 (d, J = 16.4 Hz, *Ph*), 133.60 (d, J = 15.8 Hz, *Ph*), 129.11 (s, *Ph*), 128.9 (d, J = 11.5 Hz, *Ph*), 128.07 (s, *Bz*), 127.98 (d, J = 5.7 Hz, *Bz*), 125.45 (s, *Bz*), 36.64 (d, J = 11.6 Hz, *Cy*), 32.62 (d, J = 16.5, CH_2P), 29.69 (d, J = 15.2 Hz, *Cy*), 29.06 (d, J = 11.0 Hz, *Cy*), 26.92 (d, J = 11.0 Hz, *Cy*), 26.78 (d, J = 9.2 Hz, *Cy*), 26.33(s, *Cy*).

Synthesis of $[NiCl_2(PBzCyPh)_2]$, 2. For the synthesis of the coordination compound **2**, a saturated solution of $NiCl_2$ in ethanol absolute (3 mL) was added to a THF solution of (±)-benzylcyclohexylphenylphosphine, and the resulting mixture was stirred for 15 min and then concentrated in vacuo. Dark red crystals of the complex were obtained, filtered, and dried. The yield of the process was 60% (1.079 g). Anal. Calcd for $C_{38}H_{46}Cl_2NiP_2$: C, 65.73; H, 6.68. Found: C, 65.3; H, 6.6. MS-positive FAB: 657 [$(M - Cl)^+$].

Synthesis of 4. A suspension formed by 0.24 mmol of **3**, 0.24 mmol (165 mg) of dichlorobis[(±)-benzylcyclohexylphenylphosphine]nickel(II)**,** and 30 mL of THF was stirred at room temperature for 45 min, and the resulting solution was concentrated in vacuo. The solid obtained was eluted by SiO_2 column chromatography with $CHCl_3$−acetone (100:4 for **4a**, 100:2 for **4b,** and 100:4 for **4c**) as eluent. Compounds (R_C,R_P)-**4** and (R_C,S_P)-**4** (1:1 mixture of diastereoisomers) were isolated as yellow solids in a yield of 80−90%. Characterization data: **4a** ^{31}P (101.26 MHz, $CDCl_3$): δ = 39.03 s and 39.41 s. Anal. Calcd for $C_{27}H_{33}ClNPPd$: C, 59.57; H, 6.11; N, 2.57. Found: C, 59.5; H, 6.2; N, 2.5. **4b** ^{31}P (101.26 MHz, $CDCl_3$): δ = 47.3 and 43.3 s. Anal. Calcd for $C_{29}H_{37}ClNPPd$: C, 60.85; H, 6.51; N, 2.45. Found: C, 61.0; H, 6.7; N, 2.5. **4c** ^{31}P (101.26 MHz, $CDCl_3$): δ = 38.21 and 41.48 s. Anal. Calcd for $C_{31}H_{35}ClNPPd$: C, 62.63; H, 5.93; N, 2.35. Found: C, 62.8; H, 5.8; N, 2.3. MS-positive FAB: 595 [M^+].

Separation of 4a Diastereoisomers. A 1:1 mixture of diastereoisomers (R_C,R_P)-**4a** and (R_C,S_P)-**4a** (100 mg) was carefully eluted at room temperature, in a SiO_2 column (30 × 400 mm, 30 g SiO_2) with $CHCl_3$−acetone (100:2) as eluent. The second band eluted was collected in fractions of 15 mL, 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 or the methylic proton signals. The diastereoisomer (R_C,R_P)-**4a** was obtained in 84% yield (42 mg), with a de higher than 90%. Characterization data: (R_C,R_P)-**4a** ^{31}P (101.26 MHz, $CDCl_3$):

(17) It should be noted that reaction times longer than 30 min (at 15 °C) afford a yield near 100% (calculated as conversion of starting olefin), but a significant decrease in the selectivity is also observed (see entry 6).

(18) Small amounts of 2-vinylnaphthalene dimers were observed, but not significantly bigger than those contained in the recrystallized product used as starting material.

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δ = 39.03, s. ^{1}H NMR (500 MHz, $CDCl_3$): δ = 7.45−7.35 (m, 3H, aromatic), 7.30−7.20 (m, 2H, aromatic), 7.20−7.00 (br m, 5H, aromatic), 7.00−6.80 (m, 2H, H^3, H^4), 6.40 (t, $^3J_{HH}$ = 7.5 Hz, 1H, H^2), 6.19, (m, 1H, H^1), 4.45 (m, 1H, *H*CMe), 3.96 (br m, 1H, NH), 3.5−3.8 (m, 2H, CH_2), 3.36 (br m, 1H, NH), 2.30−1.25 (m, 11H, aliphatic.), 1.71 (d, $^3J_{HH}$ = 6.6 Hz, 3H, Me). (R_C,S_P)-**4a**: ^{31}P (101.26 MHz, $CDCl_3$,): δ = 39.41, s. ^{1}H NMR (500 MHz, $CDCl_3$): 7.40−7.30 (m, 3H, aromatic), 7.30−7.20 (m, 2H, aromatic), 7.20−7.00 (br m, 5H, aromatic), 6.90−6.80 (m, 2H, H^3, H^4), 6.37 (t, $^3J_{HH}$=7.5 Hz, 1H, H^2), 6.08 (m, 1H, H^1), 4.45, (m, 1H, *H*CMe), 3.96 (br m, 1H, NH), 3.6−3.8 (m, 2H, CH_2), 3.35 (br m, 1H, NH), 2.3−1.25 (m, 11H, aliphatic), 1.71 (d, $^3J_{HH}$ = 6.6 Hz, 3H, Me).

Separation of 4b Diastereoisomers. A 1:1 mixture of diastereoisomers (R_C,R_P)-**4b** and (R_C,S_P)-**4b** (100 mg) was dissolved in ether at room temperature, and the solution was cooled to 4 °C. A crystalline fraction of (R_C,S_P)-**4b** was obtained in 70% yield (35 mg), with a de higher than 95%. Characterization data: (R_C,R_P)-**4b** ^{31}P (101.26 MHz, $CDCl_3$): δ = 43.3, s. ^{1}H NMR (500 MHz, $CDCl_3$): δ = 7.60−7.00 (br m, 10H, aromatic), 6.83 (d, $^3J_{HH}$ = 7.5 Hz, 1H, H^4), 6.66 (t, $^3J_{HH}$ = 7.5 Hz, 1H, H^3), 6.29 (t, $^3J_{HH}$ = 7.5 Hz, 1H, H^2), 5.93 (t, $^3J_{HH}$ = 7.5 Hz, 1H, H^1), 3.79−3.94 (m, 2H, CH_2), 3.50 (br m, 1H, *H*CMe), 2.67 (d, $^3J_{HH}$ = 1.6 Hz, 3H, NMe), 2.61 (d, $^3J_{HH}$ = 1.6 Hz, 3H, NMe), 2.30−1.25 (m, 11H, aliphatic.), 1.63 (d, $^3J_{HH}$ = 6.6 Hz, 3H, Me). (R_C,S_P)-**4b** ^{31}P (101.26 MHz, $CDCl_3$): δ = 47.3, s. ^{1}H NMR (500 MHz, $CDCl_3$): δ = 7.60−7.00 (br m, 10H, aromatic), 6.90−6.70 (m, 2H, aromatic), 6.12 (t, $^3J_{HH}$ = 7.5 Hz, 1H, H^2), 5.50 (t, $^3J_{HH}$ = 7.5 Hz, 1H, H^1), 3.70−3.80 (m, 2H, CH_2), 3.50 (br m, 1H, *H*CMe), 2.78 (d, $^3J_{HH}$ = 1.6 Hz, 3H, NMe), 2.64 (d, $^3J_{HH}$ = 1.6 Hz, 3H, NMe), 2.30−1.25 (m, 11H, aliphatic), 1.80 (d, $^3J_{HH}$ = 6.6 Hz, 3H, Me).

Separation of 4c Diastereoisomers. A 1:1 mixture of diastereoisomers (R_C,R_P)-**4c** and (R_C,S_P)-**4c** (100 mg) was carefully eluted at room temperature, in a SiO_2 column (30 × 400 mm, 50 g SiO_2) with $CHCl_3$−acetone (100:3) as eluent. The first band eluted was collected in fractions of 25 mL, 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 or the methylic proton signals. The diastereoisomers (R_C,R_P)-**4c** and (R_C,S_P)-**4c** were obtained in 70% (35 mg) and 66% (33 mg) yield, respectively, with a de higher than 95% in both cases. Characterization data: (R_C,R_P)-**4c** ^{1}H NMR (500 MHz, $CDCl_3$): δ = 7.60 (d, J_{HH} = 8.5 Hz, 1H, aromatic), 7.50 (d, J_{HH} = 7.5 Hz, 1H, aromatic), 7.35−7.20 (m, 5H, aromatic), 7.10 (m, 2H, aromatic), 7.06 (m, 3H, aromatic), 6.91 (m, 3H, aromatic), 6.48 (dd, J_{HH} = 9 Hz, J_{PH} = 5 Hz, 1H, H^1), 5.2 (m, J_{HH} = 5.5 Hz, 1H, *H*CMe), 4.05 (br, 1H, NH), 3.88 (m, 1H, CH_2), 3.56 (br, 1H, NH), 3.54 (m, 1H, CH_2), 2.35−1.25 (m, 11H, aliphatic), 1.95 (d, J_{HH} = 6.5 Hz, 3H, Me).^{31}P (101.26 MHz, $CDCl_3$): δ = 38.3, s. Optical rotation: $[\alpha]^{20}_D$= +6.72° cm^2 g^{-1} (c = 1). (R_C,S_P)-**4c** ^{1}H NMR (500 MHz, $CDCl_3$): δ = 7.64−7.46 (m, 5H, aromatic), 7.30−7.12 (m, 9H, aromatic), 6.70 (d, J_{HH} = 8.4 Hz, 1H, H^2), 6.05 (dd, $^3J_{HH}$ = 8.6 Hz, J_{PH} = 5.2 Hz, 1H, H^1), 5.2 (m, $^3J_{HH}$ = 5.6 Hz, 1H, *H*CMe), 3.98−3.85 (br, 2H, NH, CH_2), 3.72−3,49 (br, 2H, NH, CH_2), 2.63−0.8 (m, 11H, aliphatic), 1.98 (d, $^3J_{HH}$ = 6.2 Hz, 3H, Me).^{31}P (101.26 MHz, $CDCl_3$): δ = 41.4, s. Optical rotation: $[\alpha]^{20}_D$= +41.23° cm^2 g^{-1} (c = 1).

Synthesis of [Pd(η^3-2-MeC_3H_4)Cl(PBzCyPh)], 5 (Containing Racemic Phosphine). A 100 mg (0.144 mmol) sample of dichlorobis[(±)-benzylcyclohexylphenylphosphine]-nickel(II) and 57 mg (0.144 mmol) of [Pd(μ-Cl)(η^3-2-MeC_3H_4)]$_2$ were stirred for 30 min in toluene (30 mL). The mixture was then concentrated to dryness, and the product was purified by SiO_2 column chromatography with $CHCl_3$−acetone (100:3) as eluent. A 111 mg (0.23 mmol) sample of compound **5** was isolated as a yellow solid. Yield: 81%. Characterization data for **5**: Anal. Calcd for $C_{23}H_{30}ClPPd$: C, 57.63; H, 6.30**.** Found: C, 57.7; H, 6.3. ^{31}P (101.26 MHz, $CDCl_3$): δ = 33.5 s and 32.3 s. ^{1}H NMR (200 MHz, $CDCl_3$): δ = 7.40−7.31 (m, 10H, Ar), 7.08 (m, 6H, Ar), 7.00−6.95 (m, 4H, Ar), 4.45 (m, J_{HH} = 3.5 Hz, J_{PH} = 6.5 Hz, 2H, H^a), 3.65−3.48 (m, 4H, CH_2), 3.44 (dd, J_{PH} = 10 Hz, 2H, H^b), 2.95 (s, 1H, H^c) 2.89 (s, 1H, H^c), 2.44 (s, 1H, H^d) 2.03 (s, 1H, H^d), 2.26−1.07 (m, 22H, aliphatic), 1.86 (s, 3H, Me), 1.76 (s, 3H, Me). MS-positive FAB: 443 [(M − Cl)$^+$].

Synthesis of [Pd(η^3-2-MeC_3H_4)Cl(PBzCyPh)], 5 (Containing Optically Pure Phosphine). A 0.16 mmol (0.067 g) sample of 1,2-bis(diphenylphosphino)ethane (dppe) was added to a solution of (R_C,S_P)-**4c** or (R_C,R_P)-**4c** (0.16 mmol) in ether (30 mL), and the mixture was stirred under nitrogen for 15 min at room temperature. A 33.5 mg (0.084 mmol) sample of [Pd(μ-Cl)(η^3-2-MeC_3H_4)]$_2$ was added to the resulting suspension, and the mixture was stirred for 30 min at room temperature and then concentrated in vacuo. The solid obtained was eluted by SiO_2 column chromatography with $CHCl_3$−acetone (100:3) as eluent. Compound **5**, containing optically pure phosphine, was isolated as a yellow solid in a yield of 85% (65 mg). Optical rotation, (S_P)-[Pd(η^3-2-MeC_3H_4)Cl(PBzCyPh)]: $[\alpha]^{20}_D$= −22.2° cm^2 g^{-1} (c = 0.55).

Synthesis of [Pd(η^3-2-MeC_3H_4)($NCCH_3$)(PBzCyPh)]-[BF_4], 6. A few drops of acetonitrile and 0.104 g (0.53 mmol) of $AgBF_4$ were added to a solution of **5**, 0.240 g (0.50 mmol) in 25 mL of THF. The mixture was stirred for 15 min in the darkness, and the AgCl formed was filtered off through Celite. The resulting solution was concentrated, and the addition of ether caused the precipitation of a white solid (**6**), which was separated by filtration. Yield: 0.185 g (0.32 mmol, 65%). Characterization data for **6**: Anal. Calcd for $C_{25}H_{33}BF_4NPPd$: C, 52.52; H, 5.82; N, 2.45. Found: C, 52.3; H, 5.9; N, 2.6. ^{31}P (101.26 MHz, $CDCl_3$): δ = 34.1 s and 33.0 s. ^{1}H NMR (200 MHz, $CDCl_3$): δ = 7.52−7.40 (m, 10H, aromatic), 7.22−7.14 (m, 6H, aromatic), 7.05−6.95 (m, 4H, aromatic), 4.90 (dd, J_{HH} = 3.0 Hz, J_{PH} = 5.0 Hz, 1H, H^a), 4.85 (dd, J_{HH} = 3.0 Hz, J_{PH} = 5.0 Hz, 1H, H^a), 3.65−3.46 (m, 6H, CH_2, H^b), 3.05 (s, 1H, H^c) 2.98 (s, 1H, H^c), 2.32 (s, 1H, H^d), 2.29 (s, 6H, $NCCH_3$), 2.17 (s, 1H, H^d), 2.35−0.90 (m, 22H, aliphatic), 1.90 (s, 3H, Me), 1.69 (s, 3H, Me).

Hydrovinylation Reactions. Hydrovinylation reactions were performed in a stainless steel autoclave fitted with an external jacket connected to a thermostated isobutanol bath controlled to ±0.5 °C; internal temperature and pressure as a function of time were registered with a Linseis L-200 recorder. A mixture of **5** (20.0 mg, 4.17 × 10^{-2} mmol), $AgBF_4$ (8.9 mg, 4.57 × 10^{-2} mmol), and styrene (4.34 g, 0.0417 mol) in 10 mL of dry CH_2Cl_2 was stirred for 5 min in the darkness. After filtering off the AgCl formed the solution was placed in the autoclave and thermostated at the desired temperature, and ethylene was admitted until a pressure of 15 bar was reached. After the time indicated in Table 4 for every reaction, the autoclave was slowly depressurized and 10% HCl (10 mL) was added, and the mixture was stirred for 10 min in order to quench the catalyst. The CH_2Cl_2 layer was decanted off and dried with Na_2SO_4. The quantitative distribution and ee of the products were determined by GC analysis. Major components were characterized by ^{1}H NMR.

Characterization of Hydrovinylation Products. 3-Phenyl-1-butene: ^{1}H NMR (200 MHz, $CDCl_3$): δ = 1.36 (d, J = 7.0 Hz, 1H), 3.47 (m, 1H), 5.03 (dd, J = 10.5 Hz, J = 1.4 Hz, 1H), 5.05 (dd, J = 17.0 Hz, J = 1.4 Hz, 1H), 6.01 (ddd, J = 17.0 Hz, J = 10.5 Hz, J = 6.8 Hz, 1H), 7.10−7.35 (m, 5H). ^{13}C NMR (50.3 MHz, $CDCl_3$): δ = 20.7, 43.2, 113.1, 126.1, 127.2, 128.4, 143.2, 145.5. *cis*-2-Phenyl-2-butene: ^{1}H NMR (200 MHz, $CDCl_3$): δ = 1.77 (d, J = 6.9 Hz, 3H), 2.01 (s, 3H), 5.85 (q, J = 6.9 Hz, 1H), 7.10−7.40 (m, 5H). ^{13}C NMR (50.3 MHz, $CDCl_3$): δ = 14.3, 15.4, 122.4, 125.5, 126.4, 128.1, 135.5, 144.0. 3-(2-Naphthyl)-1-butene: ^{1}H NMR (200 MHz, $CDCl_3$): δ = 1.45 (d, J = 7.0 Hz, 1H), 3.63 (m, 1H), 5.12 (m, 2H), 6.08 (ddd, J = 17.2, J = 10.5 Hz, J = 1.4 Hz, 1H), 7.20−7.95 (m, 7H). *cis*-2-(2-Naphthyl)-2-butene: ^{1}H NMR (200 MHz, $CDCl_3$): δ = 1.63

Table 5. Summary for Crystal Data and Structure Analysis

	(R_C,S_P)-**4b**	**5**
formula	$C_{29}H_{37}ClNPPd$	$C_{23}H_{30}ClPPd$
fw	572.44	479.32
crystal Size (mm)	0.38 × 0.35 × 0.08	0.30 × 0.20 × 0.06
color, shape	yellow, plate	yellow-plate, prism
cell measurements (24 ref)	12.7° < 2θ < 15.3°	13.9° < 2θ < 18.4°
crystal system	orthorhombic	monoclinic
space group	$P2_12_12_1$ (No. 19)	$P2_1/n$ (No. 14)
cell params	a = 16.497(6) Å	a = 14.6206) Å
	b = 16.928(5) Å	b = 17.149(6) Å
	c = 9.795(6) Å	c = 9.669(6) Å
		β = 90.17°
volume	2735(2) Å^3	2424(3) Å^3
Z	4	4
density (calcd)	1.390 g cm^{-3}	1.313 g cm^{-3}
λ(Mo Kα)	0.71069 Å	0.71069 Å
μ(Mo Kα)	8.42 cm^{-1}	9.35 cm^{-1}
F(000)	1184.00	984
abs corr	DIFABS	DIFABS
transmission factors	0.837−1.148	0.829−1.168
standards number, interval	3 ref, 100 ref	3 ref, 100 ref
decay (%)	−2.40	−6.70
temperature	290(1) K	290(1) K
scan method	ω/2θ	ω/2θ
scan speed (ω)	4° min^{-1}	4° min^{-1}
2θ interval	5° < 2θ < 50.1°	5° < 2θ < 50.1°
no. of measured reflns	2439	3945
no. of unique reflns	2439	3945
no. of obsd reflns ($I > 3\sigma$)	1634	2526
no. of params	203	235
refln/param ratio	8.05	10.75
refinements	full-matrix ls on F	Full-matrix ls on F
R^a	0.0441	0.0485
R_w ($w = \sigma_F^{-2}$)^b	0.0526	0.0636
gof	1.506	1.987
residual peaks (e/Å^3)	+0.36, −0.43	+1.25, −0.62

^{a} $R = \Sigma(|F_o| - |F_c|)/\Sigma(|F_o|$. ^{b} $R_w = [(\Sigma w(|F_o| - |F_c|)^2/\Sigma wF_o^2)]^{1/2}$.

(d, J = 6.3 Hz, 3H), 1.92 (s, 3H), 5.82 (m, 1H), 7.00−7.80 (m, 7H). ^{13}C NMR (50.3 MHz, $CDCl_3$): δ = 14.4, 15.3, 123.0, 123.7, 124.2, 125.2, 125.8, 127.4, 127.5, 127.9, 129.4, 132.6, 133.5, 141.0.

The ee of the products was determined by GC analysis. 3-Phenyl-1-butene (He flow: 2.10 mL/min, 60 °C), retention times: *R*-isomer, 8.0 min; *S*-isomer, 8.2 min. 3-(2-Naphthyl)-1-butene (He flow: 2.10 mL/min, 100 °C), retention times: *R*-isomer, 38.7 min; *S*-isomer, 39.7 min. The assignment of the absolute configuration of the major enantiomers was performed by measuring the optical rotation of a reaction mixture and comparison of the sign of the obtained value with literature values.[21]

Crystallographic Studies. A yellow plate crystal of (R_C,S_P)-**4b** (0.35 × 0.08 × 0.38 mm) or **5** (0.20 × 0.06 × 0.30 mm) was selected, mounted on a glass fiber, and transferred to a Rigaku AFC6S diffractometer. Graphite-monochromatized Mo Kα radiation was used. Cell constants were obtained from a least-squares refinement using the setting angles of 25 carefully centered reflections. The system was determined to be orthorhombic, space group $P2_12_12_1$ (acentric) for (R_C,S_P)-**4b** and monoclinic, space group $P2_1/n$ (No. 14) for **5**. The data were collected using the ω−2θ scan method. The intensities of three standard reflections were measured after 100 reflections to apply the decay correction. Lorentz−polarization and absorption corrections (DIFABS method) were also applied. A summary of experimental details is given in Table 5. The structures were solved by the Patterson method. Hydrogen atoms in the π-allyl ligand were found in a difference Fourier map, and the others were included in calculated positions and not refined. Final values of R = 0.044 and R_w = 0.053 were obtained for (R_C,S_P)-**4b** and final values of R = 0.049 and R_w = 0.064 were obtained for **5**. All calculations were carried out using the TEXSAN software package on a VAX 3520 computer at the "Servicio Central de Ciencia y Tecnologia de la Universidad de Cádiz".[22]

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Supporting Information Available: Crystallographic data (excluding structure factors) for (R_C, S_P)-**4b** and **5**. This material is available free of charge via the Internet at http://pubs.acs.org

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