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A Resolution of Monodentate P* Chiral Phosphine

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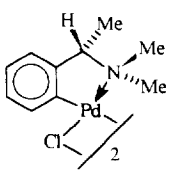
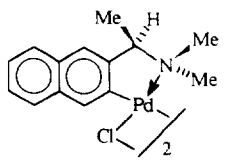
Abstract. The monodentate phosphine PMeBu^{t}Ph is obtained in enantiopure form by using a new N*-chiral ortho-palladated resolving agent; some advantages of the latter over its N-achiral analogue are shown. The conditions of resolved phosphine displacement from individual diastereomers of palladium(II) complexes are elaborated which allow the starting resolving agent to be recovered.

INTRODUCTION

Resolution of P*-chiral and atropoisomeric ligands by the use of homochiral ortho-palladated compounds **1a-3a** is a research area of considerable current interest[1-3]. The reagents of this type have many advantages over other known optically active complexes tested so far as resolving agents[4]: availability of starting homochiral amines, their facile ortho-palladation, a high stability of dimeric and mononuclear diastereomeric complexes of this type and the possibility to have crystalline solids.



(S_C)-**1a**



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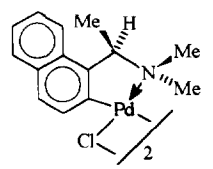


(R_C)-**3a**

Unfortunately, this method of resolution has a number of shortcomings. 1) As a rule, it is based on the solubility difference between two internally diastereomeric complexes which can not be predicted; the selectivity of complexation is not used. 2) When optical resolution is carried out under the conditions which allow the preferable selection of one of two enantiomers of a substrate[1] a total dechelation of resolving agent by the excess of phosphine was assumed to occur, which raises concerns over resolving agent stability. 3) All known methods of resolved phosphine ligand isolation result in palladacycle degradation or transformation into the nonreactive form. Only in the case of aminoarsines can the resolving agent be recovered due to the displacement of resolved ligand by ethane-1,2-diamine (En)[2]. Unfortunately, this approach did not work for aminophosphine ligands.

Recently we have devoted some effort to solve these problems by means of structural modification of complexes **1a**, **2a** and by improvements of the resolution scheme using *tert*-butylmethylphenylphosphine (P*) as a representative of monodentate phosphines. The first problem listed above was solved by means of N*-

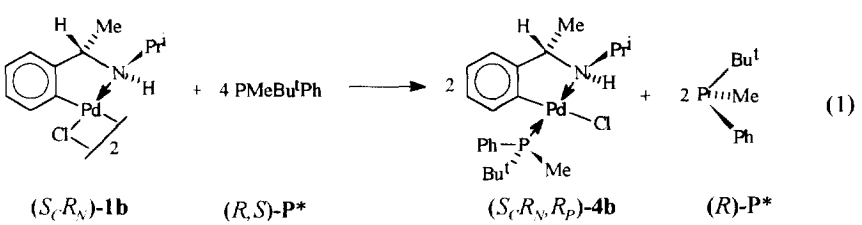
stereocentre incorporation into the palladacycle of the resolving agent. Our spectral investigations of P* bonding stereochemistry in solution have revealed that N*-chirality of palladacycle plays a crucial role in the chiral recognition despite *trans*-position of N*- and P*-stereocentres[5]. The same set of experiments has shown that problems associated with the opening of palladacycle can be avoided or diminished due to the replacement of tertiary amino group with secondary amino group[6].

Here we present our results concerning the solution of the last problem, namely, we have found the conditions of resolved phosphine displacement which allow the regeneration of starting resolving agent and we have illustrated an improved resolution scheme using a new N*-chiral resolving agent.

RESULTS

The choice of μ-chloro bridged dimeric ortho-palladated N-isopropyl-α-methylbenzyl-amine (S_CR_N)-**1b** as the best resolving agent for *tert*-butylmethylphenylphosphine (P*) was based on the following grounds. 1) This complex displays a very high level of chiral discrimination in P* bonding in solution: the equilibrium constant K between two diastereomers of monophosphine adducts **4b** was found to be equal 15.7[5]. It is important that the diastereomer (S_CR_N,R_P)-**4b** of monophosphine adduct which predominates in the solution is at once a less soluble one[7]. 3) The presence of the secondary amino group in palladacycle lowers the dechelation extent down to *ca* 13%[6]. 4) The starting homochiral N-isopropyl-α-methylbenzylamine is available from the commercial (*S*)-α-methylbenzylamine in a rather high yield (87%) in one step reaction; its direct palladation by Li_2PdCl_4 is also highly productive (84%)[8].

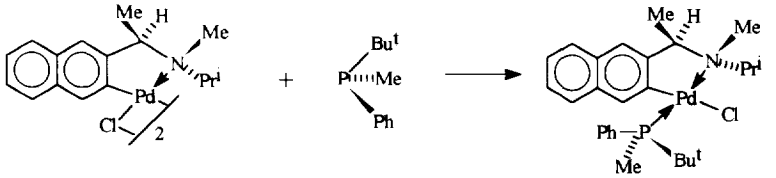
The resolution scheme employed is based on Tani's approach[1], but includes some essential modifications. The procedure consists of five steps.



(S_CR_N)-**1b** (*R,S*)-**P*** (S_CR_N,R_P)-**4b** (*R*)-**P*** (1)

1. In the first stage of P* resolution pure (S_CR_N,R_P)-diastereomer of monophosphine adduct **4b** was isolated in 73% yield after the reaction of μ-chloro dimer (S_CR_N)-**1b** with racemic phosphine P* in 1:4 molar ratio in toluene; only one recrystallization was employed. For comparison, the use of the known N-achiral analogue (S_C)-**1a** affords the mixture of two diastereomers (S_C,R_P)-**4a**/(S_C,S_P)-**4a** in *ca* 1:1 ratio (0.5% *de*)[1], which separation is a very difficult problem[7].

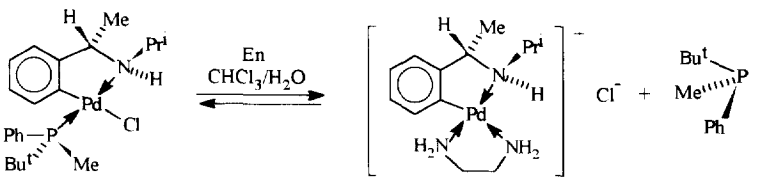
2. The second step consists of the isolation of free phosphine P* enriched with (*R*)-enantiomer which remains in mother liquor after the isolation of predominant diastereomer (S_CR_N,R_P)-**4b**. Instead of distillation[1] we have used the chromatographic purification of free phosphine. This modification allows thermal racemization to be avoided and results in removal of the residual complex **4b** which is a very highly soluble compound. Because this complex is a 6.5:1 mixture of (S_CR_N,R_P)-**4b** and (S_CR_N,S_P)-**4b** diastereomers (74% *de*) its removal was thought to result in certain increase of optical purity of uncoordinated phosphine (R_P)-P*. Unfortunately, both enantiomeric purity (63% *ee*) and chemical yield (84%) of free phosphine were found to be only moderate probably due to the oxidation of phosphine on the silica and insufficient exact reagent ratio in the microscale experiment. The estimation of chemical yield and enantiomeric purity of uncoordinated phosphine was made by ^{1}H NMR after the conversion of a small portion of phosphine into its adduct **5c** by the reaction with the dimer complex (R_CS_N)-**2c**.



$(R_C S_N)$-**2c** (*R*)-**P*** $(R_C S_N, S_P)$-**5c**

(2)

3. The most important step of phosphine resolution was its displacement from the pure diastereomer $(S_C R_N, R_P)$-**4b**. Our attempts to use diamine En for this purpose under the described conditions (the treatment by 6-fold excess of En followed by the precipitation by NH_4PF_6 [2]) have failed. The success was achieved after the increase of diamine excess up to 300-fold and due to the use of chloroform/water two-phase system. The efficient transfer of water soluble ionic complex $(S_C R_N)$-**6b** into the aqueous phase with the free phosphine remaining in organic layer leads to the complete shift of equilibrium to the product (TLC data).

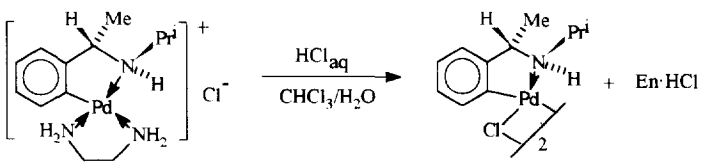


$(S_C R_N, R_P)$-**4b** $(S_C R_N)$-**6b** (H_2O) (*S*)-**P*** $(CHCl_3)$

(3)

Both the chemical yield (up to 85%) and enantiomeric purity (complete according to ^1H NMR data) of isolated phosphine were determined by above mentioned method (see eq. 2 and exp.), after the transformation of phosphine into the adduct $(R_C S_N, R_P)$-**5c**.

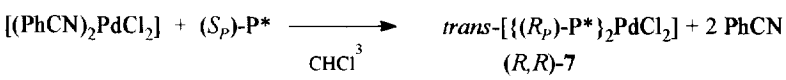
4. The regeneration of starting dimer $(S_C R_N)$-**1b** as the last step of the resolution was performed by the known method[2]; it was isolated in enantiomeric pure state in the yield of 81-83%.



$(S_C R_N)$-**6b** $(S_C R_N)$-**1b**

(4)

5. To illustrate the possibility of direct trapping of highly air-sensitive homochiral phosphine in the form of suitable precatalyst we have used the $[Pd(PhCN)_2Cl_2]$ complex as a trapping agent.



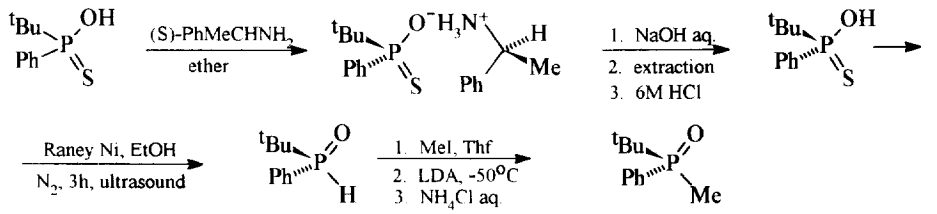
(5)

Optically active complex *trans*-$[Pd\{(R_P)$-PMeBu^{t}Ph$\}_2Cl_2]$ (**7**) was obtained in a yield of 85% and identified by TLC and ^{31}P NMR spectra by the reference to authentic sample.

DISCUSSION

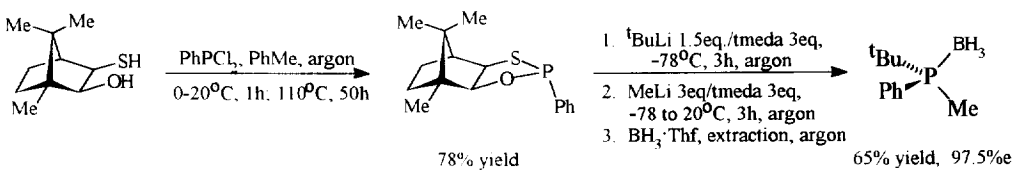
Now that we have presented our methodology of monodentate phosphine resolution there is a need to compare it with alternative routes to P*-chiral compounds (primarily to *tert*-butylmethylphenylphosphine). There are two main pure organic approaches:

(A) Stereospecific transformations of homochiral phosphorus(V) compounds pre-resolved into tertiary phosphine[9], its borane complex[10,11], phosphine oxide[11-15], or sulfide[16]. The best result so far obtained is illustrated below (Scheme 1)[15]:



Scheme 1

(B) Asymmetric synthesis of homochiral cyclic precursor, namely oxathiaphospholidine[17], oxazaphospholidine[18], or borane complex of the latter[19], followed by stereospecific introduction of required substituents. The best route is shown below[17]:



Scheme 2

The chief disadvantage of both A, B approaches is multistep procedures of conversion of expensive starting homochiral compound into the target phosphine: 3-5 steps are required as a rule for the preparation of tertiary phosphine precursor (oxide or borane complex) or 4-6 steps if considered is their potential conversion into the free phosphine. This results in a high time and reagents consumption, and causes the total yield to fall down to 10-30% under unfavourable conditions[10,13] or to ca. 50% according to the best schemes[15,17]. By contrast our methodology is the shortest two-step process of preparation of homochiral phosphine from racemic one in the total yield of 62% in microscale experiments under unoptimized conditions[20].

In the case of A, B approaches the situation is complicated (often seriously) by the fact that the P* stereocentre is affected directly during the most of transformations used. As a consequence the enantiomeric purity of starting homochiral compound may be decreased (down to 12% ee under adverse circumstances[11] or to 97.5% ee in the best scheme[17]) and additional purification is required[17-19]. Our methodology uses after resolution the decoordination process only which retains the optical purity of homochiral precursor completely.

The most of the known schemes includes a number of highly air sensitive[9,12,17] and smelling bad[9,12,14-16] intermediates and chiral auxilliary[17], required a special care during manipulation and storage. The only intermediate in our scheme, palladium(II) complex **4b**, is a crystalline air-stable solid[21], it may be prepared in principle in multigramm quantities using standard Schlenk technique (if the isolation of the second enantiomer of phosphine can be neglected) and used as a convenient form for homochiral phosphine storage. The dimer μ-chloro-bridged resolving agent (S_CR_N)-**1b** is also high stable compound. On the contrary, the free *tert*-butylmethylphenylphosphine is an extremely air-sensitive compound (cf. [12]), therefore we have reduced to a

minimum manipulations with it by means of the procedure of its direct trapping after displacement from the precursor ($S_C R_N, R_P$)-**4b**[20].

An important advantage of our methodology is that it is based on the usage of resolving agent equally available in either enantiomer form. To note, in the pure organic approaches involving natural menthol[10,11,13] or camphor[17] derivatives as chirality sources the usage of their unnatural enantiomers is possible also, but is far more expensive. The use of a rather expensive palladium(II) based resolving agent in our methodology is compensated to a large extent by the effective procedure of its recovering (81-83% in microscale experiments without optimization). To compare, chiral camphor derived reagent used in asymmetric synthesis of *tert*-butylmethylphenylphosphine was recovered in 76% yield[17].

The drawback of a number of the known organic routes to *tert*-butylmethylphenylphosphine is that both chemical and optical yields are very sensitive to steric hindrances[11,18]. On contrary, the high steric demands of one of substituents in phosphine ligand is a desirable condition of high enantiomeric discrimination during the complexation process[5].

Finally, our methodology offers a very simple route to the control of optical purity during the resolution process by using ^{1}H or ^{31}P NMR spectra of ortho-palladated precursor ($S_C R_N, R_P$)-**4b** or through the another adduct formation after phosphine displacement, for example, **5c**. To compare, the most of other approaches requires the use of HPLC on chiral columns[17,19], or additional auxilliary for ^{1}H NMR control[13-15,22].

The methodology reported herein seems to be generally applicable because it is based on the effective enantiomeric discrimination during the complexation process. It may be realized also in multigramm scale using the more simple experimental technique of Schlenk in the cases of less air-sensitive alkyldiaryl- and triarylphosphines[23] and essentially improved due to the optimization of conditions.

CONCLUSION

We have elaborated, for the first time, the conditions of free phosphine displacement from individual diastereomers of palladium complexes which allow the homohiral resolving agent to be recovered. Such modification of known resolution procedure through the internally diastereomeric ortho-palladated complexes makes this method (the shortest of all known) much less expensive. This work has demonstrated also some advantages of the use of N*-chiral ortho-palladated complex as a reagent for the resolution of monodentate phosphine as compared to its known N-achiral analogue.

EXPERIMENTAL

General. All reactions involving free phosphine were performed on a vacuum line (10^{-2} torr) in home-made glassware using prepurified argon and solvents. The silica gel for chromatographic purification of free phosphine was evacuated (10^{-2} torr) at 60°C for 3 d. and blown with dried and desoxygenated argon.

Routine ^{1}H NMR spectra were recorded at 400 MHz on a Varian VXR 400 instrument in CD_2Cl_2 or $CDCl_3$ at room temperature using tetramethylsilane as an internal standard. The ^{31}P NMR spectra were registered on a Varian FT-80A spectrometer (32.2 MHz) at -80°C or at r.t. using 85% H_3PO_4 as an external standard. Optical rotations were measured with a VNIEKI-Prodmush AI-EPO polarimeter in a 0.25-dm cell at 20°C.

Complex $[Pd(PhCN)_2Cl_2]$ was preparated as described[24]. *tert*-Butylmethylphenylphosphine was obtained as reported previously[7]. $(+)_D$-($S_C R_N$)-Di-μ-chlorobis{2-[1-isopropylamino)ethyl]phenyl-C,N}dipalladium(II) (S_C)-**1b** was synthesized by known method[8] in the yield of 84%, m.p. 198-199°C (decomp.), $[\alpha]_D^{20}$ +124 (c 0.85, chloroform). $(-)_D$-($R_C S_N$)-Di-μ-chlorobis{3-[1-(N-methyl-N-isopropylamino)ethyl]-2-naphthyl-C^2,N}-dipalladium(II) ($R_C S_N$)-**2c** was prepared as reported[25] by using 5-fold excess of AcONa as the base in the yield of 76%, m.p. 179-182°C (decomp.), $[\alpha]_D^{20}$ -290 (c 0.85, chloroform).

Resolution of (*R,S*)-*tert*-butylmethylphenylphosphine.

1) Isolation of (S_CR_N,R_P)-chloro[2-{1-(isopropylamino)ethyl}phenyl-C,N]{*tert*-butylmethylphenylphosphine}palladium(II) (4b) and (R_P)-*tert*-butylmethylphenylphosphine. The dimeric complex (S_CR_N)-**1b** (1.744 g, 2.87 mmol) was placed in the reaction vessel with the small spherical thin-walled glass phial containing racemic phosphine **P*** (2.066 g, 11.46 mmol) and magnetic stirrer. The apparatus was connected to the vacuum line, toluene (20 mL) was vacuum-transferred onto the reagents, and phial with phosphine was broken by magnetic stirrer. After the stirring for an hour at room temperature the reaction mixture was concentrated by evaporation to the volume of 3 mL and pentane (30 mL) was vacuum-transferred onto it. The resulting colourless crystalline precipitate was transferred onto the glass sinter, the vessel was filled with argon and the mother liquor was chromatographed on the short column packed with silica gel. Then the precipitate and column were washed with pentane (5 x 20 mL) which was previously vacuum-transferred into the vessel. After this procedure the eluates containing free (R_P)-**P*** phosphine were collected and concentrated in receiver which was sealed off.

The optical purity (86% *de*) of diastereomer (S_CR_N,R_P)-**4b** isolated in 81% yield was determined by ^{1}H NMR (400 MHz, CD_2Cl_2) using the integral intensities of aromatic C^6H signal.

^{1}H NMR (CD_2Cl_2), major diastereomer (S_CR_N,R_P)-**4b**: δ 1.18 (d, 3H, $^3J_{HH}$ 6.4 Hz, CHMe$_2$), 1.27 (d, $^3J_{PH}$ 14.8 Hz, 9H, PBu^t), 1.49 (d, 3H, $^3J_{HH}$ 6.4 Hz, CHMe$_2$), 1.62 (d, $^2J_{PH}$ 9.0 Hz, 3H, PMe); 1.91 (d, $^3J_{HH}$ 6.4 Hz, 3H, α-CHMe), 2.93 (m, 1H, CHMe$_2$), 3.42 (br.m, 1H, NH), 4.05 (m, 1H, α-CHMe); aromatics: 6.12 (d.d.d, 1H, $^3J_{HH}$ 7.5 Hz, $^4J_{HH}$ 1.2 Hz, J_{PH} 4.7 Hz, C^6H), 6.53 (d.t, 1H, $^3J_{HH}$ 7.5 Hz, $^4J_{HH}$ 1.6 Hz, C^4H), 6.81 (d.t, 1H, $^3J_{HH}$ 7.3 Hz, $^4J_{HH}$ 1.2 Hz, C^5H), 6.86 (d.d, 1H, $^3J_{HH}$ 7.4 Hz, $^4J_{HH}$ 1.6 Hz, C^3H); 7.5 (m, 3H, PPh), 7.98 (m, 2H, PPh); minor diastereomer (S_CR_N,S_P)-**4b**: δ 1.18 (d, 3H, $^3J_{HH}$ 6.4 Hz, CHMe$_2$), 1.31 (d, $^3J_{PH}$ 15.0 Hz, 9H, PBu^t), 1.46 (d, 3H, $^3J_{HH}$ 6.4 Hz, CHMe$_2$), 1.91 (d, $^2J_{PH}$ 9.0 Hz, 3H, PMe); 1.89 (d, $^3J_{HH}$ 6.4 Hz, 3H, α-CHMe), 3.04 (m, 1H, CHMe$_2$), 3.42 (br.m, 1H, NH); 4.05 (m, 1H, α-CHMe); aromatics: 6.22 (m, 1H, C^6H), 6.38 (m, 1H), 6.72 (m, 1H), 6.88 (m, 1H), 7.34 (m, 3H, PPh), 7.75 (m, 2H, PPh).

After single low-temperature recrystallization (-80°C) from toluene/pentane it was obtained in optical pure state in overall 73% yield (2.021 g): m.p. 188-190°C (dec.); $[\alpha]_D^{20}$ +55 (c 0.86, CH_2Cl_2). The soluble part of diastereomeric complexes **4b** was eluated from silica gel column with benzene/acetone mixture in 5:1 ratio, the combined eluates were evaporated to dryness to give additional amount of (S_CR_N,R_P)-**4b** in 13% yield (0.361 g). Its optical purity was found to be equal 74% *de* according to ^{1}H NMR data (400 MHz, CD_2Cl_2).

2) Enantiomeric purity and chemical yield of uncoordinated (R_P)-**P*** phosphine isolated from the mother liquor were determined as follows. After the receiver with phosphine was fitted with a glass-enclosed magnetic breaker and fused to the spider tipping device, the phosphine was diluted with vacuum-transferred toluene (16 mL) and distributed between the main receiver and testing tube (precharged with the calculated excess of dimer (R_CS_N)-**2c**) and the tube was sealed off. The composition of the mixture of dimer (R_CS_N)-**2c** remained and diastereomers (R_CS_N,S_P)-**5c**/(R_CS_N,R_P)-**5c** formed was estimated on the base of ^{1}H NMR data, using the integral intensities ratio of signals of NMe, CHMe$_2$ and some of aromatic protons; the chemical yield[26] and the optical purity of (R_P)-**P*** phosphine were found to be 84% and 63% *ee*, respectively.

^{31}P NMR (CH_2Cl_2, -80°C): δ 36.18 and 35.72 ppm (~4:1 ratio);

^{1}H NMR ($CDCl_3$, 35°C), major diastereomer (R_CS_N,S_P)-**5c**: δ 0.90 (d, 3H, $^3J_{HH}$ 6.5 Hz, CHMe$_2$), 1.40 (d, $^3J_{PH}$ 15.0 Hz, 9H, PBu^t), 1.62 (d, 3H, $^3J_{HH}$ 6.8 Hz, CHMe$_2$), 1.60 (d, $^2J_{PH}$ 8.9 Hz, 3H, PMe); 2.12 (d, $^3J_{HH}$ 6.5 Hz, 3H, α-Me), 2.89 (m, 1H, CHMe$_2$), 2.69 (d, 3H, $^4J_{PH}$ 3.5 Hz, NMe), 3.98 (m, 1H, α-CHMe); aromatics: 6.58 (d, 1H, J_{PH} 6.0 Hz, C^1H), 7.09 (d, 1H), 7.2-8.1 (m, 4H from Np + 5H from PPh); minor diastereomer (R_CS_N,R_P)-**5c**: δ 0.93 (d, 3H, $^3J_{HH}$ 6.4 Hz, CHMe$_2$), 1.40 (d, $^3J_{PH}$ 14.8 Hz, 9H, PBu^t), 1.66 (d, 3H, $^3J_{HH}$ 6.7 Hz, CHMe$_2$), 2.04 (d, $^2J_{PH}$ 9.7 Hz, 3H, PMe); 2.10 (d, $^3J_{HH}$ 6.5 Hz, 3H, α-Me), 3.00 (m, 1H, CHMe$_2$), 2.70 (d, 3H, $^4J_{PH}$ 3.5 Hz, NMe), 3.98 (m, 1H, α-CHMe); aromatics: 6.42 (d, 1H, J_{PH} 6.0 Hz, C^1H), 6.95 (d, 1H), 7.2-8.1 (m, 4H from Np + 5H from PPh); excess of dimer (R_CS_N)-**2c** (the mixture of cis/trans-isomers): δ 2.5 (s, NMe), 2.60 (s, NMe); 1.05 m (CHMe$_2$).

3) The displacement of the enantiopure (S_P)-P* phosphine from the pure diastereomer (S_CR_N,R_P)-4b. The pure diastereomer (S_CR_N,R_P)-IIa (0.101 g, 0.21 mmol) and magnetic stirrer were placed into the reaction tube and desoxygenated in vacuo. After chloroform (6 mL) was vacuum-transferred into the tube, pre-desoxygenated aqueous solution (15 mL) of the excess of ethane-1,2-diamine (3.78 g, 63 mmol) was added and the tube was sealed off. The reaction mixture was vigorously stirred for 2 h at r.t., the organic layer was transferred into the Na_2SO_4 containing tube of another apparatus which was sealed off (the aqueous phase was used for the regeneration of resolving agent). After the solution of phosphine was dried for 2 h, the solvent and En admixture were removed in vacuo, the pure chloroform was vacuum-transferred on the phosphine remained in the tube, the solution was filtered through the glass sinter into the another tube containing a slight excess of (R_CS_N)-2c (0.077 g, 0.105 mmol) used as a reagent for the estimation of yield and optical purity of phosphine P*. The composition of the mixture of (R_CS_N,R_P)-5c formed and excess of reagent (R_CS_N)-2c remained was determined by means of ^{1}H NMR spectra: the chemical yield[26] and the optical purity of phosphine were calculated as 85% and 100% *ee*, respectively.

^{1}H NMR ($CDCl_3$, 35°C) of (R_CS_N,R_P)-5c: δ 0.91 (d, 3H, $^3J_{HH}$ 6.4 Hz, CHMe$_2$), 1.39 (d, $^3J_{PH}$ 14.8 Hz, 9H, PBu^t), 1.63 (d, 3H, $^3J_{HH}$ 6.7 Hz, CHMe$_2$), 2.02 (d, $^2J_{PH}$ 9.7 Hz, 3H, PMe); 2.09 (d, $^3J_{HH}$ 6.5 Hz, 3H, α-Me), 2.98 (m, 1H, CHMe$_2$), 2.69 (d, 3H, $^4J_{PH}$ 3.5 Hz, NMe), 3.97 (m, 1H, α-CHMe); aromatics: 6.42 (d, 1H, J_{PH} 6.0 Hz, C^{1}H), 6.95 (d, 1H), 7.2-8.1 (m, 4H from Np + 5H from PPh); excess of dimer (R_CS_N)-2c (the mixture of cis/trans-isomers): δ 2.48 (s, NMe), 2.54 (s, NMe); 1.01 m (CHMe$_2$).

4) Homochiral phosphine (S_P)-P* trapping. By the same way, starting from 0.113 g (0.233 mmol) of diastereomer (S_CR_N,R_P)-4b and 4.398 g (730 mmol) En, but using the complex [Pd(NCPh)$_2$Cl$_2$] (0.043 g, 0.11 mmol) as the trapping agent the homochiral complex *trans*-[{(R_P)-P*}$_2$PdCl$_2$], (R_P,R_P)-7, was obtained in 85% yield (0.053 g): m.p. 112-113°C, R_f 0.75 (Silufol, benzene-acetone 5:1); ^{31}P NMR (CH_2Cl_2): δ 19.68 ppm (s).

The mixture of *meso*- {(R_P,S_P)-7} and racemic form {(R_P,R_P)*-7} of complex *trans*-[P*$_2$PdCl$_2$] was prepared from the racemic phosphine P* under the described for other phosphines conditions[27] in the yield of 65%: m.p. 182-184°C, R_f 0.75 (Silufol, benzene-acetone 5:1); ^{31}P NMR (32.2 MHz, CH_2Cl_2): δ 19.66 (s) and 19.72 ppm (s) in 1:1 ratio. Anal. Calcd. for $C_{22}H_{34}Cl_2P_2Pd$: C, 49.16; H, 6.33. Found: C, 49.19; H, 6.38.

5) The regeneration of the resolving agent. The aqueous solution of cationic complex (S_CR_N)-6b, remained after the separation of phosphine was treated with 2N HCl (pH 3-4) and chloroform (10 mL). After the vigorous stirring for 5 min, the organic layer was separated, dried over Na_2SO_4 and evaporated to dryness in vacuo. The crude dimer (S_CR_N)-1b was purified on the column of silica gel (*L*5/40, *h* 10 cm, *d* 2 cm, eluent benzene-acetone 7:1) and recrystallized from chloroform/hexane. The yield 83% (0.053 g), R_f 0.61 (Silufol, benzene-acetone 7:1); $[\alpha]_D^{20}$ +124 (c 0.83, $CHCl_3$); lit. data[9]: $[\alpha]_D^{20}$ +125 (c 0.85, $CHCl_3$).

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