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A resolution of the monodentate P*-chiral phosphine $PBu^tC_6H_4Br$-4 and its NMR-deduced absolute configuration

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Abstract

Both enantiomers of the monodentate phosphine $PBu^tC_6H_4Br$-4 were obtained in an enantiopure state by chromatographic separation of their diastereomeric adducts with a new homochiral *ortho*-palladated resolving agent derived from α-*tert*-Bu-substituted tertiary benzylamine. The conformation of the palladacycle and the absolute configuration of the phosphine were determined using ^1H NMR spectroscopy (including NOE technique) and confirmed by an X-ray diffraction study of both diastereomeric complexes. The enantiomers of the resolved phosphine were displaced from the individual diastereomers of the palladium(II) complexes with recovery of the starting resolving agent, and trapped in the form of binuclear coordination complexes of palladium(II). © 1999 Published by Elsevier Science Ltd. All rights reserved.

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1. Introduction

Contrary to a rather wide use of homochiral *ortho*-palladated compounds for resolution of bi- and polydentate P*-chiral phosphine ligands,[1,2] the precedents for application of this method to monodentate phosphine resolution,[3–5] including P*-chiral ones,[3] remain rather rare. In addition to the possibility of direct uses of monodentate P*-chiral phosphines as ligands for enantioselective catalysis,[6] they may also serve as chiral synthons for the preparation of diverse bi- and polydentate phosphine ligands using well elaborated methods.[7]

Several advantages of this route to diverse P*-chiral ligands may be mentioned. First of all, there is the possibility to recover a rather expensive *ortho*-palladated resolving agent either via resolved monodentate

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phosphine displacement by a bidentate diamine,[3c] or through its direct transfer from the palladacycle to the more inert metal centre.[5b] In the instance of bi- and polydentate ligands, it remains impossible to date. Furthermore, the neutral nature of *ortho*-palladated adducts with monodentate phosphines offers the opportunity to use chromatography at the stage of diastereomeric derivatives separation instead of their recrystallization commonly used in the case of cationic diphosphine adducts.[1,2] To note, such a chromatographic approach was introduced in practice for the first time by one of us in 1992[8] and was only rarely and with moderate success used later.[5b,9]

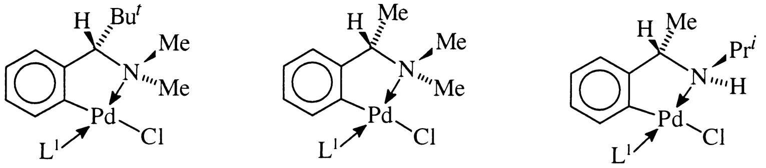
The resolution of any monodentate phosphine by homochiral palladacycles requires a more efficient resolving agent (compared to that required for the bidentate analogues) because high rotameric lability of monodentate ligands is expected, which may drastically decrease the energy difference between the two diastereomeric adducts. Probably, this may be the reason that the first attempts to resolve monodentate diaryl- and triarylphosphines using α-methyl-substituted palladacycles were of low efficiency.[3d,e]

Here, we describe the resolution of monodentate P*-chiral ligand *tert*-butylphenyl(4-bromophenyl)phosphine $PBu^tC_6H_4Br$-4 (L^1) using a new *ortho*-palladated matrix (S_C,S_C)-**1** derived from tertiary α-*tert*-Bu-substituted benzylamine.[10] The absolute configuration of the palladium-coordinated phosphine was determined by ^1H NMR spectroscopy (including NOE techniques) using homochiral palladacycle as a reference point and supported by an X-ray study of both diastereomeric adducts. Several examples of this problem's solution, using NOE techniques[11] or NMR-chemical shift regularities,[12] are known. However, until now this approach has been applied only to bidentate ligands.

2. Results and discussion

2.1. Phosphine resolution

The choice of homochiral dimer (S_C,S_C)-**1** as an optimal resolving agent for the preparation of enantiopure phosphine L^1 was made after the TLC screening[13] of several diastereomeric pairs of *ortho*-palladated adducts (S_C,R_P)-**2a**–**4a**/(S_C,S_P)-**2b**–**4b** differing by the side chain structure (Scheme 1).



(S_C,R_P)-**2a**
(S_C,S_P)-**2b**

(S_C,R_P)-**3a**
(S_C,S_P)-**3b**

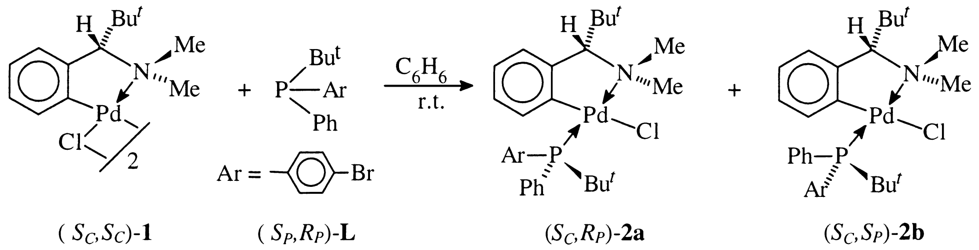
(S_CR_N,R_P)-**4a**
(S_CR_N,S_P)-**4b**

ΔR_f = 0.13 0.05 < 0.03

Scheme 1.

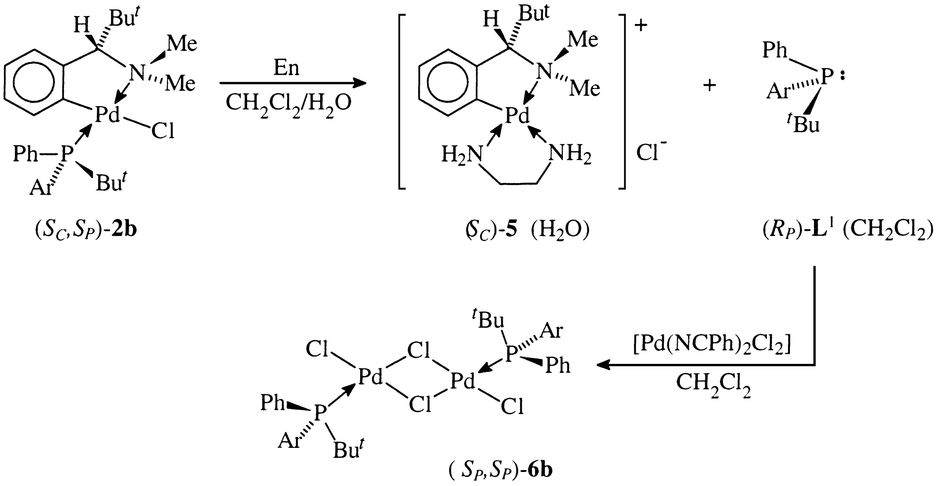
It is to be noted, that the *ortho*-palladated matrix (S_C,S_C)-**1** was previously shown to be a more efficient derivatizing agent (compared to two other palladacycles) for the determination of the enantiomeric purity of monodentate phosphines.[14]

The procedure of the phosphine L^1 resolution includes the interaction of dimer (S_C,S_C)-**1** with a slight excess of the racemic phosphine ligand in deoxygenated benzene at room temperature (Scheme 2). Subsequent column chromatography of the (S_C,R_P)-**2a**/(S_C,S_P)-**2b** mixture affords both diastereomers in the total yield of 80% in a diastereomerically pure state. The structures and complete diastereomeric purity of complexes **2a**,**b** were confirmed by ^{1}H and ^{31}P{^{1}H} NMR spectroscopy: the spectrum of each of two diastereomers contains only one signal (^{31}P) or one set of signals (^{1}H NMR).



Scheme 2.

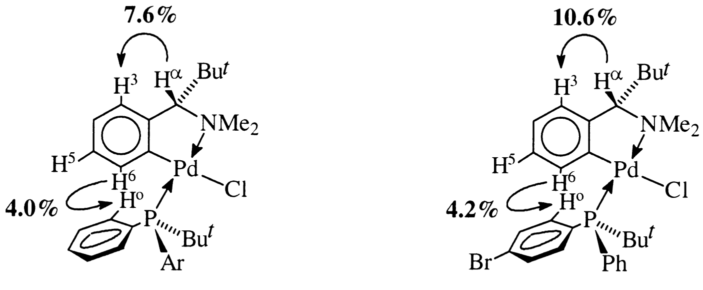
The scheme of resolved phosphine isolation employed here is similar to that described previously[3c] with only minor modifications (Scheme 3).



Scheme 3.

It consists of the following steps: (i) the complete displacement of the free phosphine from the individual diastereomer (S_C,R_P)-**2a** or (S_C,S_P)-**2b** was achieved by the introduction of excess ethylenediamine in a dichloromethane/water two-phase system. The chelating agent excess could be diminished down to the 100-fold, compared to the 300-fold excess required for the removal of the phosphine PMeBu^{t}Ph (L^2) previously studied,[3c] due to a weaker coordination of diarylalkylphosphine L^1 to palladium(II) compared to that of aryldialkylphosphine L^2; (ii) to avoid a partial loss of valuable enantiopure phosphine during its isolation, we used a methodology of direct trapping in the form of binuclear bis(phosphine) palladium(II) complexes (R_P,R_P)-**6a** or (S_P,S_P)-**6b** suitable for the further use as precatalysts; and (iii) the regeneration of the starting dimer (S_C,S_C)-**1** from the cationic diamine intermediate (S_C)-**5** was performed in the yield of 92% by diamine protonation under the standard conditions.[3c,15]

Binuclear complexes **6a**,**b** exist in solution as a mixture of *syn*/*anti*-isomers in a ca. 3:1 ratio. The *syn*-isomer reveals a fluxional behavior,[16] probably due to a more restricted rotameric mobility of the bulky phosphine ligand (cf. lit.[17]).



(**a**) (**b**)

Figure 1. The NOE-derived assignments of the protons of palladated phenylene group for the (S_C,R_P)-**2a** (a), and (S_C,S_P)-**2b** diastereomers (b). The similar NOE contacts between the C^6H proton and the *ortho*-protons of the other P-aryl substituent (3.2 and 4.2%, respectively) are omitted for clarity (see Fig. 3).

2.2. Solution structure of diastereomeric complexes **2a**,**b**

The main goal of this part of our work was: (i) to estimate the conformation of benzylaminate palladacycle in the both diastereomeric complexes; and (ii) to find convenient ^1H NMR criteria for the determination of the absolute configuration of monodentate P*-chiral phosphines. The solution to both problems required the reliable assignment of all palladacycle and phosphine signals which was performed on the basis of the homonuclear decoupling and NOE techniques.

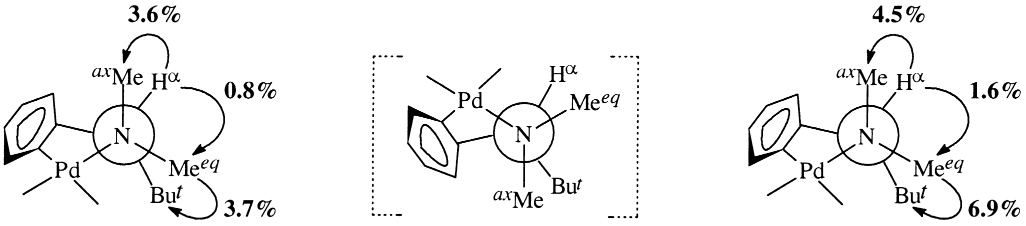
trans(P,N)-Geometry of **2a**,**b** complexes may be useful for the identification of the protons of the phenylene group. (i) The expected influence of the P-aromatic ring anisotropy makes it possible to suppose that two high-field resonances (δ 5.98–6.01 and 6.18–6.21 ppm[18]) originate from the C^6H and C^5H protons of the palladated phenylene moiety, respectively. (ii) A rather large ^{31}P–^1H coupling constant found for the most high-field signal (J_{HP} 6.9–6.6 Hz) supports its assignment to the C^6H proton adjacent to the palladation site. (iii) The observed NOE interactions between the C^6H and *ortho*-protons of both P-aryl substituents gave the most reliable confirmation of this conclusion (see Fig. 1). In the case of both isomers **2a**,**b**, irradiation of the C^6H proton leads to 4.0–3.8 and 3.2–4.2% enhancement for the PPh and PAr-groups, respectively.

Furthermore, the C^3H proton of phenylene group was also clearly identified by the NOE technique. The irradiation of the benzylic α-CH proton gave a rather large enhancement (7.6–10.6%) for the most low-field one-proton signal at δ 6.82–6.84 ppm (Fig. 1). For both diastereomeric complexes, all the aromatic protons of the phenylene group reveal as distinct well-resolved signals of the expected multiplicity. The sequence of their chemical shifts (from high to low fields for C^6H–C^3H protons) remains unchanged, which is typical for phosphine adducts of *ortho*-palladated benzylamines.[19] This trend may be successfully used for the assignment of proton signals of the palladated phenylene group in the spectra of related complexes.

Two diastereotopic NMe groups of palladacycle reveal as a broad singlet at δ 2.62–2.64 ppm and doublet at δ 2.99 ppm (J_{HP} 3.1–3.3 Hz). The 'a priory' assumption about the more efficient spin–spin coupling of the equatorial N-substituent with the *trans*-located ^{31}P nuclei[20a] allows us to assign these two signals to the axial and equatorial N-substituents, respectively.

2.2.1. Palladacycle conformation

The palladacycle conformation in diastereomers **2a**,**b** was determined using NOE techniques and the spin–spin coupling analysis. Commonly, the $^4J_{HP}$ constant for the α-methine proton serves as the main criteria for this problem solution.[20] A large value of this constant (reflecting an efficient spin–spin



$\lambda(S_C)$-**2a** $\delta(S_C)$ $\lambda(S_C)$-**2b**

(a) (b) (c)

Figure 2. Newman projections[24] of (S_C)-palladacycle along the N–C(α) bond for NOE-derived $\lambda(S_C)$-conformation for (S_C,R_P)-**2a** (a) and (S_C,S_P)-**2b** (b) diastereomers, and that for alternative $\delta(S_C)$ conformations (c)

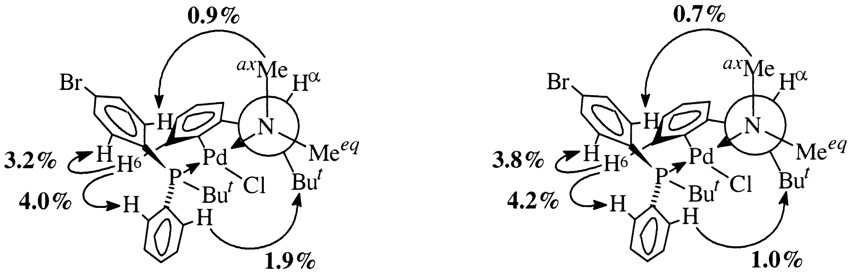
coupling with the ^{31}P nuclei via nearly coplanar chain of H–C–N–Pd–P bonds) is indicative of the equatorial orientation of the α-C–H bond in the $\lambda(S_C)$ or $\delta(R_C)$ conformation. For example, magnitudes $^4J_{HP}$ 5.8–6.3 Hz[21] were reported for the phosphine adducts of *ortho*-palladated *N*,*N*-dimethyl-1-(1-naphthyl)ethylamine existing only in $\lambda(S_C)$ or $\delta(R_C)$ conformations.[22] On the contrary, $^4J_{HP}$ values from 0 up to 6.5 Hz were observed for the two diastereomers of more conformationally flexible derivatives of α-methylbenzylamine where both conformations, with equatorial and axial α-Me groups are available.[23] In the case of both diastereomers **2a**,**b** this resonance appears as a doublet at δ 3.24–3.25 ppm with the identical values of $^4J_{HP}$ 5.4 Hz, that permits us to suppose that the palladacycle adopts the $\lambda(S_C)$ conformation in both complexes.

The detailed examination of NOE data in terms of Newman projections (see Fig. 2[24]) provides direct support for this conformation.

(i) The observed interactions between the α-methine proton and both NMe groups are possible only in the $\lambda(S_C)$ stereochemistry. In the alternative $\delta(S_C)$ conformation, only one interaction of this kind (with equatorial NMe group) is predictable; (ii) furthermore, in the case of $\lambda(S_C)$ conformation, an axial NMe group should be closer to the α-methine proton than an equatorial one (in crystal dihedral angles 42.1–46.4 and 70.5–74.6°, respectively). The observed difference between the NOE enhancements for the axial and equatorial NMe groups after irradiation of α-CH proton (3.6–4.5 and 0.8–1.6%, respectively) or vice versa (4.2–3.7 and 2.7–1.7%) is in complete accordance with this prediction; and (iii) in line with assumption of the $\lambda(S_C)$ stereochemistry, a rather intense NOE signal for α-*tert*-Bu substituent under irradiation of only NMe^{eq} protons (3.7–6.9%) was detected. On the contrary, in the alternative $\delta(S_C)$ conformation the α-*tert*-Bu protons must contact both NMe groups; the α-*tert*-Bu···NMe^{ax} interaction being more pronounced.

To note, all these NOE results gave additional support for the above-mentioned assignment of singlet at δ 2.62–2.64 ppm and the doublet at δ 2.99 ppm to the axial and equatorial NMe groups, respectively.

The retention of the $\lambda(S_C)$ conformation of the benzylaminate palladacycle with an axial α-*tert*-Bu substituent in both diastereomeric complexes (S_C,R_P)-**2a** and (S_C,S_P)-**2b** independent of the (S_P) or (R_P) stereochemistry of phosphine ligand is unambiguously supported by the following data: (i) the constant $^4J_{HP}$ found for the α-CH proton has identical values (5.4 Hz) in both cases; (ii) the similar magnitudes of the NOE enhancements are observed for the corresponding protons of both diastereomeric complexes; and (iii) the chemical shifts for the appropriate protons of the palladacycle coincide almost completely ($\Delta\delta \leq 0.04$ ppm, cf. lit.[23]). To note, the same $\lambda(S_C)$ conformation was found from X-ray investigation of the starting dimer (S_C,S_C)-**1**[14] and an NMR spectral study of its mononuclear derivatives.[10]



λ(S_C,R_P)-**2a**

(a)

λ(S_C,S_P)-**2b**

(b)

Figure 3. NOE derived rotameric state of two enantiomers of monodentate phosphine L^1 coordinated to the homochiral λ(S_C)-palladacycle in the (S_C,R_P)-**2a** (a) and (S_C,R_P)-**2b** diastereomer (b)[24]

2.2.2. Rotameric state of monodentate phosphine L^1

A number of arguments allow us to conclude that the rotation of phosphine L^1 around the Pd–P bond is restricted.

(i) Statistic considerations for the free phosphine rotation lead to a prediction that the palladacycle C^6H proton should be less shielded in the case of diarylphosphines (such as L^1) than in the case of triarylphosphine ligands (for example, PPh_3). However, the C^6H resonance is more up-field shifted in the spectra of **2a**,**b** adducts compared to their PPh_3 analogue[10] (δ 5.98–6.01 and 6.30 ppm, respectively). More pronounced C^6H shielding in adducts **2a**,**b** indicates that the rotamers with the nearly orthogonal orientation of one of two P-aryl groups with respect to the palladated phenylene ring are predominant.

(ii) The same conclusion could be inferred from the NOE enhancement (3.2–4.2%) observed for the *ortho*-protons of both P-Ar and P-Ph substituents upon irradiating the palladacycle C^6H proton (and vice versa, 2.2–3.2%). On the contrary, any interactions between the C^6H and P-Bu^t protons could not be detected by NOE techniques (see Figs. 1 and 3).

(iii) The chemical shifts of the P-Ar and P-Ph group *ortho*-protons appeared to be drastically different and isomer-dependent. Only one of these resonances reveals a significant down-field shift up to δ 8.4–8.5 ppm compared to δ 7.4 ppm in the spectra of free phosphine L^1.[14] It is the *ortho*-H of the PAr group in the spectrum of diastereomer **2a**, but that of the PPh group in the case of isomer **2b**. It should be noted that this drastic nonequivalence of the two similar aryl substituents at the phosphorus atom may originate from their different positions with respect to the anisotropy domain of the metal centre[25] (see below).

All these facts indicate a rather restricted rotation of monodentate phosphine L^1 about the Pd–P bond in both diastereomers **2a**,**b** in solution. Namely, both P-Ar and P-Ph substituents are located in the proximity of the palladated phenylene ring, wherein the P-Bu^t group is oriented preferably toward the chlorine ligand.

2.2.3. Phosphine absolute configuration

The absolute configuration of the phosphine ligand could be estimated if the location of aromatic P-substituents above or below the coordination plane (in the terms of Fig. 3) would be fixed. This problem was solved using the axial NMe group (identified unambiguously, see above) as the point of reference.

The long-range NOE contact between the NMe^{ax} group and the *ortho*-protons of only the PAr substituent (0.9% enhancement, see Fig. 3) was detected in the spectrum of diastereomer **2a**, while, in the case of the isomer **2b**, the same NMe^{ax} group is in a proximity of the *ortho*-protons of the PPh substituent (0.7% enhancement). These NOE interactions indicate that, in the diastereomer **2a**, both NMe^{ax} and PAr groups are located above the coordination plane, while, in the case of the isomer **2b**, the PPh group is disposed in a proximity of the NMe^{ax} group above the coordination plane. Furthermore, we also observed the NOE responses of the α-*tert*-Bu protons upon irradiation of *ortho*-H of the PPh group (1.9%) in the case of the isomer **2a**, or upon irradiation of *ortho*-H of the PAr group (1.0%) in the case of the isomer **2b**. It indicates that these groups are located below the coordination plane. As a result, the absolute configuration (S_C,R_P) should be proposed for the diastereomer **2a**, and the (S_C,S_P) configuration, for the isomer **2b**.

The anomalous low-field position of the signal of *ortho*-protons of the PAr or PPh group in the spectra of diastereomers **2a** and **2b**, respectively (δ 8.4–8.5 ppm compared to 7.57–7.50 ppm for *ortho*-H of the second P-aryl substituent and 7.4–7.6 ppm[14] for free phosphine L^1), can clarify the origin of the unusual restriction of the Pd–P rotameric mobility of monodentate phosphine L^1. To estimate the real deshielding extent per *ortho*-H, the observed down-field shift (Δδ ~0.9 ppm) should be nearly doubled because each of two *ortho*-protons of the free rotating P-aryl group spends only about half of its time in the vicinity of a deshielding source. This effect may be attributed to some kind of *ortho*-H···Pd interaction, found previously in the case of coordination compounds of palladium(II)[26] and palladium(0)[27] with arylphosphines.

It is important that the interactions PAr···Pd (**2a**) or PPh···Pd (**2b**) were detected only ‘above’ the coordination plane, i.e. for the P-aryl group *trans*-disposed with respect to the bulky α-substituent in the palladacycle. Probably, screening the alternative axial site (‘below’ the coordination plane) by the bulky α-*tert*-Bu group, is responsible for this choice. A rather large (in account of statistic considerations) down-field shift of the α-*tert*-Bu proton resonance (Δδ ~0.5 ppm) in the spectra of phosphine adducts **2a**,**b** compared to that of the free amine ligand may also be caused by their participation in the weak interaction with the metal centre.

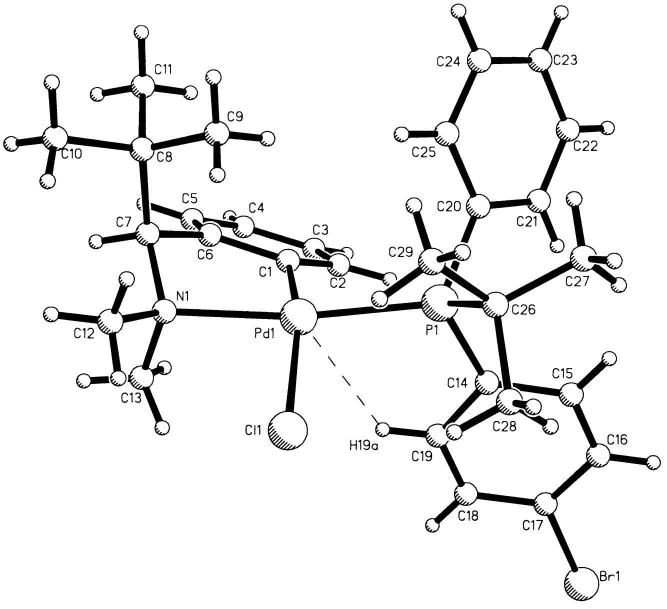
This trend may be further used as a criteria for the estimation of the absolute configuration of monodentate P*-chiral arylphosphines by means of ^{1}H NMR spectroscopy. Namely, the *trans*-position of the P-aryl group, with respect to the bulky α-substituent, may be inferred from the low-field position of its *ortho*-proton resonance.

2.3. Crystal structures of complexes **2a**,**b**

To create a more reliable basis for the further estimation of the absolute configuration of other P*-chiral arylphosphines by means of NMR spectroscopy of their adducts with homochiral palladacycles, we accomplished an X-ray diffraction study of both diastereomeric complexes **2a**,**b**. To note, cases of the X-ray comparative study for both diastereomers of *ortho*-palladated adducts with chiral ligands remain rare until now.[28]

The crystal structures of both complexes **2a**,**b** are in full accordance with the conclusions deduced from the NMR data. First of all, we confirmed unambiguously the absolute stereochemistry of diastereomers **2a**,**b**: namely, **2a** has the (S_C,R_P)-configuration, while **2b** possesses the (S_C,S_P)-stereochemistry. Such a justification creates a reliable basis for the NMR estimation of the absolute configuration of other monodentate P*-chiral arylphosphine ligands using homochiral palladacycle as a reference point.

Complex (S_C,R_P)-**2a** exists in the crystal as two independent molecules (*1* and *2*), slightly different in their geometric parameters (Fig. 4). The most significant difference between these two molecules consists in the extent of tetrahedral distortion of the palladium coordination environment: the angle between the {C^1PdN} and {PPdCl} planes is increased up to 19.3° in molecule *1* compared to only 6.7° for molecule *2* and 11.5° for the other diastereomer (S_C,S_P)-**2b** (Fig. 5). The first value seems to be an extremely large one; only one example of nearly the same distortion (19.2°) may be found among



Selected bond lengths (Å) and angles (deg.)

Pd(1)-C(1)	2.012(7)
Pd(1)-N(1)	2.174(6)
Pd(1)-P(1)	2.276(2)
Pd(1)-Cl(1)	2.409(2)
N(1)-C(13)	1.457(11)
N(1)-C(12)	1.504(10)
N(1)-C(7)	1.513(10)
P(1)-C(14)	1.820(7)
P(1)-C(20)	1.841(8)
P(1)-C(26)	1.908(7)
C(1)-Pd(1)-N(1)	80.6(3)
C(1)-Pd(1)-P(1)	94.9(2)
N(1)-Pd(1)-P(1)	171.9(2)
C(1)-Pd(1)-Cl(1)	159.4(2)
N(1)-Pd(1)-Cl(1)	90.3(2)
P(1)-Pd(1)-Cl(1)	96.03(8)

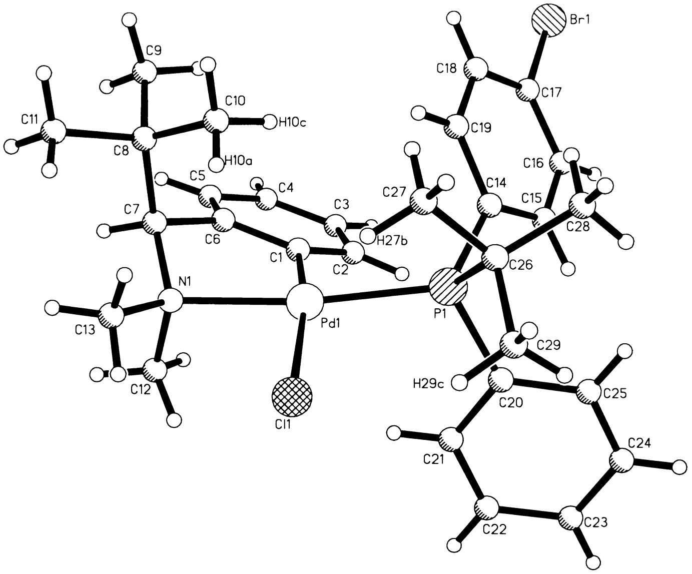
Figure 4. X-Ray structure of diastereomer (S_C,R_P)-**2a** (molecule *1*): $C_{29}H_{38}BrClNPPd$, M 653.33, monoclinic space group $P2_1$, *a* 12.151(2)Å, *b* 15.249(3) Å, *c* 15. 883(3) Å; β 90. 94(2)°, *V* 2942. 6(9) $Å^3$, *Z* 4; d_{calc} 1.475 g cm^{-3}, Mo-K_α radiation, 293 K; the final *R* and R_w values are 0.0314 and 0.0750, respectively, for 5607 independent reflections corrected for absorption by a Ψ-scan curve

the α-methylbenzylamine-derived cyclopalladated adducts with monodentate phosphole possessing biphenyl backbone[5e]; somewhat higher tetrahedral distortions (20.1–20.8°) were observed for two related derivatives with sterically overcrowded axially dissymmetric biphenyl-2,2′-diphosphines.[12a,20b]

It seems to be especially important that the palladacycle in both diastereomers (S_C,R_P)-**2a** and (S_C,S_P)-**2b** adopts in the crystal the same λ(S_C)-conformation independent of the stereochemistry of coordinated phosphine. The bulky α-*tert*-Bu group is located in the axial position: the angle between the α-C–C(Bu-*tert*) bond and the normal to the mean coordination plane (m.c.pl.) are equal to 9.1–6.9 and 177.4 (or 2.6)° for (S_C,R_P)-**2a** and (S_C,S_P)-**2b** diastereomers,[29] respectively. The palladacycle puckering is somewhat more pronounced in the structure of diastereomer (S_C,R_P)-**2a** compared to isomer (S_C,S_P)-**2b**: the total sum of the intrachelate angles are equal to 141.2–140.7 and 135.7°, respectively. A similar trend is observed for the phenylene ring twisting regarding the m.c.pl. (35.8–28.3 and 28.6° for **2a**,**b**, respectively).

The next important result is that the phosphine rotameric state is in full accordance with the predictions based on the NMR data. The functions of two P-aryl substituents in the structure of each of the diastereomers **2a**,**b** may be divided and denoted as one ‘Pd-interacting’ group and a second ‘phenylene ring shielding’ group.

Only one of two P-aryl substituents in each of the diastereomers may be considered as the ‘Pd-interacting’ one. In the structure of diastereomer (S_C,R_P)-**2a** it is the PAr group, while, in the case of (S_C,S_P)-**2b**, it is the PPh group. Several arguments may be presented in support of this idea. (i) This P-aryl substituent oriented nearly orthogonal to the mean coordination plane with the almost fixed angle between P–C(aryl) bond and normal to the m.c.pl.: equal to 24.2–21.4° (for PAr in **2a**) or 25.3° (for PPh in **2b**); (ii) one of the *ortho*-hydrogens of the P-aryl group of this kind is directed strictly to the metal centre with the torsion angle $PdPC^{ipso}C^{ortho}$ equal to 2.6–5.8°, compared to 47.1–59.8° for the second aryl substituent at the phosphorus atom; (iii) from the analysis of the nearest environment of palladium



Selected bond lengths (Å) and angles (deg.)

Pd(1)-C(1)	2.000(4)
Pd(1)-N(1)	2.162(4)
Pd(1)-P(1)	2.2785(14)
Pd(1)-Cl(1)	2.3940(13)
N(1)-C(13)	1.497(6)
N(1)-C(12)	1.500(6)
N(1)-C(7)	1.503(6)
P(1)-C(14)	1.827(4)
P(1)-C(20)	1.822(5)
P(1)-C(26)	1.901(4)
C(1)-Pd(1)-N(1)	79.2(2)
C(1)-Pd(1)-P(1)	96.59(13)
N(1)-Pd(1)-P(1)	173.12(11)
C(1)-Pd(1)-Cl(1)	166.63(12)
N(1)-Pd(1)-Cl(1)	92.27(11)
P(1)-Pd(1)-Cl(1)	92.83(5)

Figure 5. X-Ray structure of diastereomer (S_C,S_P)-**2b**. $C_{29}H_{38}BrClNPPd$, M 653. 33, orthorhombic space group $P2_12_12_1$, *a* 10.734(4) Å, *b* 13.306(3) Å, *c* 20.727(3) Å; *V* 2960.4(14) Å^3, *Z* 4; d_{calc} 1.466 g cm^{-3}, Mo-K$_\alpha$ radiation, 293 K; the final *R* and R_w values are 0.0275 and 0.0657, respectively, for 3706 independent reflections corrected for absorption by a Ψ-scan curve

atom, it became evident that the reason for such a preference in the P-substituents orientation is some kind of attractive interaction between the metal and the *ortho*-hydrogen of the aromatic ring at phosphorus: a rather short Pd···H distance was found for the *ortho*-hydrogen of the P-bromophenyl group in the case of the (S_C,R_P)-**2a** complex (2.814 and 2.661 Å for two independent molecules, respectively) or for the *ortho*-hydrogen of the P-phenyl group in the structure of the (S_C,S_P)-**2b** diastereomer (2.783 Å), compared to the sum of van der Waal's radii of these atoms equal to 3.1 Å.[30] These values lie near the lower limit of the distance range found previously in the structures of coordination compounds of palladium(II) (2.84–2.85 Å[26]) and palladium(0) (2.73–2.83 Å[27]) with P-arylphosphines; and (iv) a rather significant reduction of the PC(*ipso*)C(*ortho*) *endo*-angle involving the C–H fragment participating in the interaction C–H···Pd compared to the corresponding *exo*-angle of the same aromatic ring (by 7.2° for PAr group in **2a** and 6.2° for PPh substituent in **2b**) may be used as additional evidence in the favor of attractive nature of *ortho*-H···Pd interaction.

The orientation of the second P-aryl substituent (non-participating in the interactions with the metal centre) seems to be optimal for the efficient deshielding of the proton of the palladated phenylene group adjacent to the metallation site, namely H^{2A} in the X-ray notations. The *ipso*-carbon atom of the PPh group in the **2a** structure, or of the PAr ring in the case of the diastereomer **2b**, is much closer to the H^{2A} atom (*ipso*-C···H^{2A} distance equal to 2.80–2.58 and 2.570 Å for the **2a** and **2b** isomers, respectively: that is, less than the sum of van der Waals radii 3.0 Å[30]) compared to that for alternative ('Pd-interacting') P-aryl substituent (*ipso*-C···H^{2A} distance 2.97–3.30 Å). However, both P-aryl rings of this kind retain the possibility of free rotation about the *ipso*-C–P bond, as it becomes evident from a wide variation of interplane angles {C_6H_4}/{ArP} or {C_6H_4}/{PhP} from 49.9° for isomer **2b** up to 96.8–102.6° in the case of complex **2a**. This orientation of alternative P-aryl groups, altogether with their proximity to the palladated phenylene ring, allow us to consider that they are the main source of shielding phenomenon observed for the C(6)H and C(5)H protons of the phenylene ring in the NMR spectra of **2a**,**b** diastereomers.

To note, in accordance with the NOE data, the *tert*-BuP group takes nearly the same eclipsed orientation in both diastereomers **2a**,**b** with the angle of 50–57° in regard to the normal to the m.c.pl. at the same side as that occupied by the α-*tert*-Bu group.

A close proximity of the phosphorus atom to the C^6H proton was also confirmed by the X-ray study of **2a**,**b** diastereomers; the $C^6H\cdots P$ distances (2.882–2.971 and 2.985 Å, respectively) are shorter than the sum of van der Waal's radii of these atoms (3.0 Å).[30]

3. Conclusion

This work has demonstrated a number of advantages of dimer (S_C,S_C)-**1**'s use as a reagent and the chromatographic methodology of monodentate phosphines resolution: (i) dimer (S_C,S_C)-**1** is more suitable for the resolution of ligand L^1 possessing a very low asymmetry extent (two P*-aryl substituents are different only at the periphery of a molecule) than other dimers tested; (ii) the chromatographic procedure of diastereomeric *ortho*-palladated adducts separation affords both pure enantiomers of phosphine in a high yield in one experiment; (iii) the displacement of diarylalkylphosphine L^1 from the precursor (S_C,R_P)-**2a** or (S_C,S_P)-**2b** requires less of an excess of ethane-1,2-diamine compared to that in the case of aryldialkylphosphine; (iv) the high-yield recovery of starting dimer (S_C,S_C)-**1** compensates, to a large extent, for a use of rather expensive palladium(II)-based resolving agent; and (v) the manipulations with the air-sensitive phosphine L^1 are reduced to a minimum by means of its direct trapping in the form of the corresponding binuclear coordination complexes **5a**,**b**.

A series of important results was obtained during the ^{1}H NMR and X-ray study of both diastereomeric adducts (S_C,R_P)-**2a** and (S_C,S_P)-**2b**: (i) the retaining of the same λ(S_C) conformation of the α-*tert*-Bu substituted palladacycles in both diastereomers is indicative of the conformational rigidity of the new matrix; (ii) the monodentate phosphine bonded with the palladacycle is not flexible in contrast to widespread opinion; a rotation about the Pd–P bond is restricted due to some kind of attractive interaction of *ortho*-H of one of the P-aryl groups with the palladium centre which reveals in low-field shift of their resonance in ^{1}H NMR spectra; and (iii) these interactions create a reliable basis for the NMR spectral determination of the arylphosphine absolute configurations using homochiral palladacycles as a reference point because a bulky α-*tert*-Bu substituent remains free only one of two axial positions at the metal after screening the other axial site.

4. Experimental

4.1. General

All reactions involving free phosphine were performed under argon using the Schlenk and syringe technique. The solvents were purified by standard methods and distilled under argon before use. Routine ^{1}H NMR spectra were recorded at 400 MHz on a Varian VXR 400 instrument in $CDCl_3$ (if otherwise not indicated) at room temperature using tetramethylsilane as an internal standard; the assignments were made using homonuclear decoupling experiments and NOE technique.[31] The ^{31}P NMR spectra were registered on a Varian VXR 400 (161.9 MHz) or Varian FT-80A spectrometer (32.2 MHz) at room temperature 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)$_2$Cl$_2$] was prepared as described.[32] *tert*-Butylphenyl(4-bromophenyl)phosphine (L^1) was obtained as reported previously.[14] Starting dimer (+)$_D$-(S_C,S_C)-di-μ-chlorobis{2-[1-(dimethylamino)neopentyl]phenyl-*C*,*N*}dipalladium(II), (S_C,S_C)-**1**, was synthesized by a known method[10] in the yield of 83%, mp 185–188°C (decomp.), R_f 0.91 (Silufol, benzene:acetone, 5:1); $[\alpha]_D^{20}$ +255 (*c* 0.40, chloroform).

4.2. *Resolution of (*R,S*)-*tert*-butylphenyl(4-bromophenyl)phosphine (L^1)*

4.2.1. *Separation of (*S$_C$,R$_P$*)-**2a** and (*S$_C$,S$_P$*)-**2b** diastereomers of chloro[2-{1-(dimethylamino)-neopentyl}phenyl-*C,N*]{*tert*-butylphenyl(4-bromophenyl)phosphine-*P*}palladium(II)*

The dimeric complex (S_C,S_C)-**1** (0.373 g, 0.561 mmol) was dissolved in benzene (6 mL) and poured into a Shlenk bulb. The solution formed was deoxygenated and phosphine L^1 (0.361 g, 1.12 mmol) was added by syringe. After stirring for 15 min at room temperature the reaction mixture was evaporated to dryness. Single preparative flash-column chromatography (*h*=15 cm, *d*=3 cm; Silpearl) using an ether:heptane (1:1) mixture as eluent gave chromatographically pure diastereomeric complexes (S_C,R_P)-**2a** (0.300 g, 0.459 mmol) and (S_C,S_P)-**2b** (0.280 g, 0.429 mmol) in the yields of 82 and 76%, respectively, as light-yellow crystals in the diastereomerically pure state (according to ^{1}H NMR data). The fractions containing the diastereomers **2a**,**b** mixture did not exceed 8 mg (1.1%); they may be separated by repeated column chromatography. The analytically pure samples of both diastereomers **2a**,**b** were obtained by their recrystallization from a dichloromethane–heptane mixture.

Diastereomer (S_C,R_P)-**2a**: mp 182–183°C (dec.); $[\alpha]_D^{20}$ +165.8 (*c* 0.6, chloroform); R_f 0.51 (Silufol, ether:heptane, 1:1, three-fold elution). Anal. calcd for $C_{29}H_{38}BrClNPPd$: C, 53.31; H, 5.86; N, 2.14. Found: C, 53.57; H, 5.82; N, 1.92; ^{31}P NMR (CDCl$_3$, 162 MHz): δ 56.09 ppm (s); ^{1}H NMR (CDCl$_3$); palladacycle signals: δ 1.424 (s, 9H, α-CMe$_3$), 2.624 (br.s, 3H, $^4J_{HP}$ <1 Hz, NMe^{ax}), 2.989 (d, 3H, $^4J_{HP}$ 3.1 Hz, NMe^{eq}), 3.236 (d, $^4J_{HP}$ 5.4 Hz, 1H, α-CH); 5.984 (ddd, 1H, J_{HP} 6.9 Hz, $^3J_{HH}$ 7.4 Hz, $^4J_{HH}$ 0.8 Hz, C^{6}H), 6.177 (dt, 1H, $^3J_{HH}$ 7.4 Hz, $^4J_{HH}$ 1.1 Hz, C^{5}H), 6.616 (dt, 1H, $^3J_{HH}$ 7.3 Hz, $^4J_{HH}$ 0.8 Hz, C^{4}H), 6.818 (dd, 1H, $^3J_{HH}$ 7.4 Hz, $^4J_{HH}$ 1.1 Hz, C^{3}H); phosphine signals: δ 1.403 (d, 9H, $^3J_{HP}$ 16.8 Hz, PBu^t), 8.377 (dd, 2H, $^3J_{HP}$ 10.2 Hz, $^3J_{HH}$ 8.5 Hz, *ortho*-H of the PC$_6$H$_4$Br-4 group); 7.700 (dd, 2H, $^3J_{HH}$ 8.5 Hz, *meta*-H of the PC$_6$H$_4$Br-4 group); 7.576 (ddd, 2H, $^3J_{HP}$ 10.2 Hz, $^3J_{HH}$ 8.5 Hz, $^4J_{HH}$ 1.1 Hz, *ortho*-H of the PPh group); 7.183 (dt, 2H, $^3J_{HH}$ 7.3 Hz, $^4J_{HH}$ 1.4 Hz, *meta*-H of the PPh group); 7.249 (dt, 1H, $^3J_{HH}$ 7.4 Hz, $^4J_{HH}$ 1.9 Hz, *para*-H of the PPh group).

Diastereomer (S_C,S_P)-**2b**: mp 182–183°C (dec.); $[\alpha]_D^{20}$ +136.7 (*c* 0.6, chloroform); R_f 0.37 (Silufol, ether:heptane, 1:1, three-fold elution). Anal. calcd for $C_{29}H_{38}BrClNPPd$: C, 53.31; H, 5.86; N, 2.14. Found: C, 53.75; H, 5.63; N, 1.89; ^{31}P NMR (CDCl$_3$, 162 MHz): δ 56.743 ppm (s); ^{1}H NMR (CDCl$_3$); palladacycle signals: δ 1.420 (s, 9H, α-CMe$_3$), 2.638 (br.s, 3H, $^4J_{HP}$ <1 Hz, NMe^{ax}), 2.991 (d, 3H, $^4J_{HP}$ 3.3 Hz, NMe^{eq}), 3.246 (d, $^4J_{HP}$ 5.4 Hz, 1H, α-CH); 6.013 (ddd, 1H, J_{HP} 6.6 Hz, $^3J_{HH}$ 7.7 Hz, $^4J_{HH}$ 1.1 Hz, C^{6}H), 6.214 (dt, 1H, $^3J_{HH}$ 7.6 Hz, $^4J_{HH}$ 1.3 Hz, C^{5}H), 6.643 (dt, 1H, $^3J_{HH}$ 7.4 Hz, $^4J_{HH}$ 1.1 Hz, C^{4}H), 6.837 (dd, 1H, $^3J_{HH}$ 7.4 Hz, $^4J_{HH}$ 1.6 Hz, C^{3}H); phosphine signals: δ 1.401 (d, 9H, $^3J_{HP}$ 15.1 Hz, PBu^t), 7.500 (dd, 2H, $^3J_{HP}$ 9.7 Hz, $^3J_{HH}$ 8.5 Hz, *ortho*-H of the PC$_6$H$_4$Br-4 group); 7.317 (dd, 2H, $^3J_{HH}$ 8.5 Hz, $^4J_{HP}$ 1.4 Hz, *meta*-H of the PC$_6$H$_4$Br-4 group); 8.472 (ddd, 2H, $^3J_{HP}$ 10.9 Hz, $^3J_{HH}$ 7.7 Hz, $^4J_{HH}$ 1.7 Hz, *ortho*-H of the PPh group); 7.57 (m, 3H, *meta*-H and *para*-H of the PPh group).

4.2.2. *The displacement of the enantiopure phosphine L^1 from the individual diastereomers **2a**, **2b** and its trapping*

4.2.2.1. *Di-μ-chlorodichlorobis{(*R$_P$*)-*tert*-butylphenyl(4-bromophenyl)phosphine-*P*}dipalladium(II), (*R$_P$,R$_P$*)-**6a**.*

The pure diastereomer (S_C,R_P)-**2a** (0.020 g, 0.031 mmol) was dissolved in dichloromethane (5 mL) in a three-necked bulb equipped with condenser, magnetic stirring bar and argon inlet, and deoxygenated in vacuo. Then pre-deoxygenated aqueous solution (5 mL) of the 100-fold excess of ethane-1,2-diamine (0.184 g, 3.0 mmol) was added and the reaction mixture was vigorously stirred for 0.5 h at room temperature. The organic layer was separated from the aqueous one (used further for dimer **1** recovery, see below), dried over the sodium sulfate, filtered under argon in an isolated system and evaporated to dryness in vacuo to remove the solvent and the remainder of diamine and to afford a free phosphine (S_P)-L^1. To the solution of the latter in dichloromethane (6 mL) the equimolar amount of bis(benzonitrile)palladium(II) chloride (0.012 g, 0.031 mmol) was added, the reaction mixture was stirred for 0.5 h and concentrated in vacuo to the volume of 2–3 mL. Preparative chromatography on short 'dry column'[33] (Silpearl, h=2 cm, d=2 cm, benzene:acetone, 10:1) was used to separate a slight excess of starting complex [Pd(PhCN)$_2$Cl$_2$]; it gave the title complex **6a** in the yield of 92% (0.0141 g, 0.0141 mmol) as an orange-yellow amorphous powder: mp 145–150°C (dec.); $[\alpha]_D^{20}$ −14.8 (c 0.3, dichloromethane); R_f 0.61 (Silufol, ether:heptane, 10:1). Anal. calcd for $C_{32}H_{36}Br_2Cl_4P_2Pd_2$: C, 38.09; H, 3.88; P, 5.98. Found: C, 38.55; H, 3.64; P, 6.21.

^{31}P NMR (CDCl$_3$, −50°C, 32.2 MHz; two signals in 2.7:1 ratio[16]): δ 51.96 ppm (br.s, major), 43.82 ppm (s, minor); ^{1}H NMR (CDCl$_3$, 26°C, two sets of signals in ~2.8:1 ratio[16]): major isomer: δ 1.465 (br.d, 9H, $^3J_{HP}$ 16.8 Hz, PBu^t), 7.741 (br.dd, 2H, $^3J_{HP}$ 10.6 Hz, $^3J_{HH}$ 8.4 Hz, *ortho*-H of the PC$_6$H$_4$Br-4 group); 7.572 (dd, 2H, $^3J_{HH}$ 8.4 Hz, $^4J_{HP}$ 1.6 Hz, *meta*-H of the PC$_6$H$_4$Br-4 group); 7.966 (br.dd, 2H, $^3J_{HP}$ 11.2 Hz, $^3J_{HH}$ 7.8 Hz, *ortho*-H of the PPh group); 7.472 (m, 2H, *meta*-H of the PPh group); 7.541 (m, 1H, *para*-H of the PPh group); minor isomer: δ 1.452 (d, 9H, $^3J_{HP}$ 16.0 Hz, PBu^t), 7.808 (dd, 2H, $^3J_{HP}$ 10.6 Hz, $^3J_{HH}$ 8.6 Hz, *ortho*-H of the PC$_6$H$_4$Br-4 group); 8.034 (ddd, 2H, $^3J_{HP}$ 10.8 Hz, $^3J_{HH}$ 8.4 Hz, $^4J_{HH}$ 1.4 Hz, *ortho*-H of the PPh group); the remaining resonances are obscured by the signals of the major isomer.

*4.2.2.2. Di-μ-chlorodichlorobis{(*S$_P$*)-*tert*-butylphenyl(4-bromophenyl)phosphine-*P*}dipalladium(II), (*S$_P$,S$_P$*)-**6b***. Prepared similarly starting from the diastereomer (S_C,S_P)-**2b** (0.034 g, 0.052 mmol) in the yield of 91% (0.0236 g, 0.0236 mmol); mp 145–150°C (dec.); $[\alpha]_D^{20}$ 17.1 (c 0.4, dichloromethane); R_f 0.61 (Silufol, ether:heptane, 10:1). Anal. calcd for $C_{32}H_{36}Br_2Cl_4P_2Pd_2$: C, 38.09; H, 3.88; P, 5.98. Found: C, 38.55; H, 3.64; P, 6.21.

^{1}H NMR (CDCl$_3$, 26°C, two sets of signals in ~3.0:1 ratio[16]): major isomer: δ 1.466 (br.d, 9H, $^3J_{HP}$ 16.6 Hz, PBu^t), 7.742 (br.dd, 2H, $^3J_{HP}$ 10.6 Hz, $^3J_{HH}$ 8.4 Hz, *ortho*-H of the PC$_6$H$_4$Br-4 group); 7.575 (dd, 2H, $^3J_{HH}$ 8.4 Hz, $^4J_{HP}$ 1.7 Hz, *meta*-H of the PC$_6$H$_4$Br-4 group); 7.966 (br.dd, 2H, $^3J_{HP}$ 11.0 Hz, $^3J_{HH}$ 7.9 Hz, *ortho*-H of the PPh group); 7.472 (m, 2H, *meta*-H of the PPh group); 7.540 (m, 1H, *para*-H of the PPh group); minor isomer: δ 1.452 (d, 9H, $^3J_{HP}$ 15.9 Hz, PBu^t), 7.806 (dd, 2H, $^3J_{HP}$ 10.6 Hz, $^3J_{HH}$ 8.6 Hz, *ortho*-H of the PC$_6$H$_4$Br-4 group); 8.053 (ddd, 2H, $^3J_{HP}$ 10.6 Hz, $^3J_{HH}$ 8.5 Hz, $^4J_{HH}$ 1.5 Hz, *ortho*-H of the PPh group); the remaining resonances are obscured by the signals of the major isomer.

^{31}P NMR (d$_8$-toluene, 26°C, 161.9 MHz; two signals in 4.2:1 ratio[34]): δ 51.528 ppm (br.s, major), 45.179 ppm (s, minor); ^{1}H NMR (d$_8$-toluene, 26°C, 400 MHz; two sets of signals in ~4:1 ratio[16]): major isomer: δ 1.202 (br.d, 9H, $^3J_{HP}$ 16.3 Hz, PBu^t), 7.536 (br.dd, 2H, $^3J_{HP}$ 11.0 Hz, $^3J_{HH}$ 8.8 Hz, *ortho*-H of the PC$_6$H$_4$Br-4 group); 7.020 (d, 2H, $^3J_{HH}$ 8.8 Hz, *meta*-H of the PC$_6$H$_4$Br-4 group); 7.784 (br.dd, 2H, $^3J_{HP}$ 10.8 Hz, $^3J_{HH}$ 8.1 Hz, *ortho*-H of the PPh group); 6.975 (m, *meta*-H and *para*-H of the PPh group); minor isomer: δ 1.345 (d, 9H, $^3J_{HP}$ 15.5 Hz, PBu^t), 7.681 (dd, 2H, $^3J_{HP}$ 10.1 Hz, $^3J_{HH}$ 8.4 Hz, *ortho*-H of the PC$_6$H$_4$Br-4 group); 7.188 (dd, 2H, $^4J_{HP}$ 1.5 Hz, $^3J_{HH}$ 8.4 Hz, *meta*-H of the PC$_6$H$_4$Br-4 group); 8.016 (m, 2H, $^3J_{HP}$ 11.0 Hz, *ortho*-H of the PPh group); the remaining resonances are obscured by the signals of the major isomer.

4.2.3. The recovery of the resolving agent

To the aqueous solution of cationic complex (S_C)-**5**, remained after the separation of phosphine containing organic phase (see Section 4.2.2.1), dichloromethane (5 mL) was added. Then the resulting two-phase mixture was treated drop-by-drop with 2 N HCl (up to pH 3–4). After vigorous stirring for 5 min, an organic layer was separated, dried over sodium sulfate and evaporated to dryness in vacuo. It afforded the chromatographically pure dimer (S_C,S_C)-**1** in a yield of 92% (0.094 g, 0.0141 mmol), R_f 0.91 (Silufol, benzene:acetone, 5:1); mp 186–189°C (dec) (lit. data[10] mp 184–188°C (dec)); $[\alpha]_D^{20}$ 266 (*c* 0.4, CH_2Cl_2); lit. data[10] $[\alpha]_D^{20}$ 255 (*c* 0.4, $CHCl_3$).

All the X-ray structural results are available from the Cambridge Crystallographic Database.

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