Optical resolution of racemic stilbenediamine using N*-chiral *ortho*-palladated matrix*

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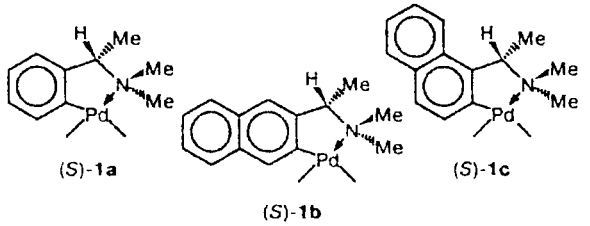
Optical resolution of racemic stilbenediamine (Stien) was performed by recrystallization of its diastereomeric adducts with *ortho*-palladated (*S*)-*N*-isopropyl-α-methylbenzylamine. The less soluble (S_CR_N,*SS*) diastereomer was studied by X-ray diffraction analysis. It was established that the crystal of this diastereomer consists of dimers formed *via* association of two molecules of the mononuclear cationic complex with an additional molecule of free diamine of the same absolute configuration. The association occurs through a system of hydrogen bonds and weak agostic interactions. Based on the X-ray diffraction data, the procedure was improved for the resolution of stilbenediamine due to the more profitable use of the *ortho*-palladated reagent. The Stien/Pd ratio in the diastereomer isolated was increased up to 3 : 2. The conformational features of the complex are discussed on the basis of ^{1}H NMR spectroscopy data.

Key words: 1,2-diamines, *ortho*-palladated complexes, optical resolution, hydrogen bonds, metallacycle conformation, X-ray diffraction analysis, nuclear Overhauser effect.

Studies carried out over the last 25 years have clearly demonstrated the considerable potential of *ortho*-palladated complexes as reagents for optical resolution of a wide diversity of substrates possessing ligand properties, namely, of mono-,[2] di-,[3a] and polyphosphines,[3b] arsinophosphines,[4] diarsines,[5] aminophosphines,[6] aminoarsines,[7] diimines,[8] iminophosphines,[9] iminoarsines,[10] mercaptophosphines,[11] mercaptoarsines,[12] amine sulfoxides,[13] phosphine sulfoxides,[14] arsine sulfoxides,[15] and aminocarboxylic acids.[16] One of the rare failures in utilization of this procedure involves an unsuccessful attempt at resolving the simplest vicinal diamine with the symmetry C_2, namely, *N*,*N*,*N*′,*N*′-tetramethyl-2,3-diaminobutane (Me_4bn).[17] It seems especially surprising that the most efficient of the three *ortho*-palladated matrices (**1a—c**) known before we started studies in this field, namely, dimer (*S*)-**1c**, was used as a resolving agent in this case.



* The preliminary results were reported previously, see Ref. 1.

Recently,[18] we have observed high stereoselectivity of complexation of *N**-chiral *ortho*-palladated compounds with monodentate phosphine PMeBu^{t}Ph, which was used for its efficient optical resolution.[19] This fact gave impetus to the estimation of the possible extension of the scope of these new matrices. In this work, we report the optical resolution of the racemic ligand with the symmetry C_2, *viz.*, 1,2-diphenylethane-1,2-diamine (Stien), using the N*-chiral *ortho*-palladated matrix, namely, the derivative of (*S*)-*N*-isopropyl-α-methylbenzylamine (S_CR_N)-**2**.

This ligand attracts ever-growing interest because Stien, its *N*-substituted analogs, and analogs substituted in Ph rings by themselves as well as their transition-metal complexes possess the high ability to discriminate enantiomers in a great diversity of processes, namely, in stoichiometric asymmetric syntheses,[20,21] in enantioselective catalysis of reduction,[22—24] oxidation,[25—27] and formation of the C—C bonds,[28—30] and in processes of optical resolution[31] and determination of the enantiomeric purity of various substrates.[32—34]

The high biological activity of platinum complexes with stilbenediamine and its Ph-substituted analogs[35—37] is also an essential spur to the development of this field. Not only does the anticancer action of some of these complexes surpass the characteristics of the known standard, namely, of *cis*-diamminedichloroplatinum(II), but it is also enantioselective. For example, the $PtCl_2$

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complex with the (*SS*) enantiomer of 1,2-bis(2-hydroxyphenyl)ethane-1,2-diamine (L^1) is more active than the related complexes with the (*RR*) and *meso* forms of the same diamine.[35] That is the reason why the development of new approaches to the optical resolution of stilbenediamine and its derivatives is a timely problem.

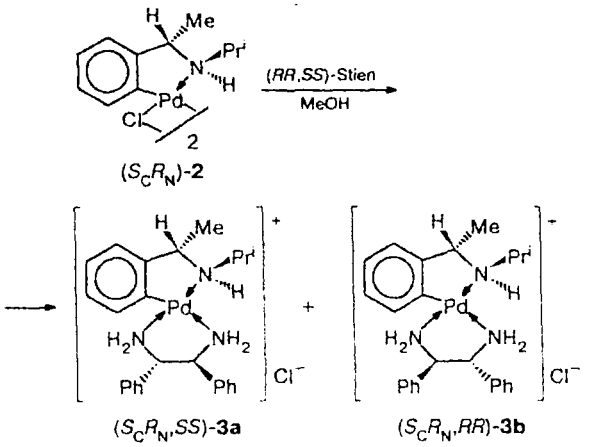
Results and Discussion

The choice of the dimeric *ortho*-palladated derivative of (*S*)-*N*-isopropyl-α-methylbenzylamine (S_CR_N)-**2** [38] as a reagent for resolution of diamine was made based on its high ability to discriminate enantiomers. In the case of complexation of dimer (S_CR_N)-**2** with racemic phosphine PMeBu^{t}Ph, the constant of equilibrium (*K*) between two diastereomers of the monophosphine adduct is 15.7.[18]

Stereochemistry of complexation in solution

First, we examined the possibility of stereoselection upon complexation of homochiral dimer (S_CR_N)-**2** with racemic diamine Stien in a solution (Scheme 1). The use of a twofold excess of diamine (Pd : Stien = 1 : 2) creates, in principle, the conditions for choosing between the enantiomers of the racemic substrate. The second necessary condition for enantioselection is the possibility of exchange between the coordinated and free diamine molecules. The ease of this intermolecular redistribution of enantiomers of ditertiary diamine Me_4bn among the diastereomeric adducts with dimer (*S*)-**1c** has been established previously.[17] We confirmed the occurrence of a similar exchange in the **3a**,**b**—Stien system by spectral methods. The addition of a slight excess of free racemic diamine Stien to a solution of the individual diastereomer of the diamine adduct, (S_CR_N,*SS*)-**3a** (its isolation is described below), resulted in the appearance of signals

Scheme 1



in the ^{1}H NMR spectra, which correspond to the second diastereomer of the diamine adduct, (S_CR_N,*RR*)-**3b**, in a statistically expected ratio.

The estimation of the composition of the reaction mixture by ^{1}H NMR spectroscopy in methanol-d_4 (see Experimental) showed that the two diastereomers of the mononuclear adduct with diamine, (S_CR_N,*SS*)-**3a** and (S_CR_N,*RR*)-**3b**, are formed in virtually equal amounts. This ratio was retained after storage of the solution for 14 days. It should be noted that the difference in the chemical shifts of the signals for the protons of the substituents at the C* and N* stereocenters of the palladacycle (α-Me- and *N*-Pr^i groups), which belong to two diastereomeric adducts **3a** and **3b** ($\Delta\delta$ = 0.015 and 0.091, respectively), is sufficiently large for the process of resolution of this diamine to be monitored by ^{1}H NMR spectroscopy.

It should be admitted that the absence of stereoselectivity, which we observed upon complexation of dimer (S_CR_N)-**2** with racemic diamine Stien in a solution, is a natural consequence of two factors. First, this is the predictable low efficiency of steric interactions between the small-volume primary amino groups of the diamine being resolved and the chiral palladacycle. A high degree of chiral discrimination, which has been observed previously upon complexation of (*S*)-**1c** with ditertiary vicinal 1,2-diamine Me_4bn,[17] was attributed primarily to steric interactions between the *cis*-arranged Me_2N groups of the palladacycle and diamine. Note that in spite of efficient enantiomeric discrimination found for the (*S*)-**1c**—Me_4bn system in a solution, an attempt to perform preparative optical resolution of diamine Me_4bn failed due to cocrystallization of two diastereomeric complexes.[17]

Destruction of the agostic interaction between the *N*-Pr^i substituent and the palladium atom in polar media may be the second possible cause of the absence of stereoselectivity. In the case of neutral complexes in nonpolar media, this interaction contributes to some extent to conformational stabilization of the palladacycle.[39—41]

Optical resolution of diamine Stien

Initially, preparative resolution of racemic diamine Stien utilizing homochiral matrix (S_CR_N)-**2** was performed with the use of a stoichiometric amount of diamine (Pd : Stien = 1 : 1). Under these conditions (method *A*, see Experimental), the less soluble diastereomer of the cationic complex, (S_CR_N,*SS*)-**3a**, was isolated after double recrystallization in an analytically pure state as a monohydrate in 51% yield (with respect to the theoretical value); the optical purity was 88% *de*. Unfortunately, all attempts to isolate the second more soluble diastereomer (both by crystallization and by chromatography) were unsuccessful.

Although this procedure for the resolution of diamine Stien is simple, it is not economically optimum

because one-half of the expensive Pd-containing reagent remained virtually unconsumed (the yield of diamine resolved was only 25% with respect to the total amount of Pd). Because of this, we attempted to enhance the efficiency of the resolving-agent usage by introducing a twofold excess of diamine (Pd : Stien = 1 : 2). In principle, under the conditions of rapid exchange of the diamine enantiomers between diastereomeric complexes **3a,b** (even if their starting ratio was 1 : 1) and a sufficiently large difference in their solubility, one would expect selective crystallization of only one of two diastereomers of mononuclear adduct **3** because its content in a solution may be replenished from reserves of free diamine.

In these experiments (method ***B***, see Experimental), the less soluble diastereomer of the complex, (S_CR_N,*SS*)-**3a**, was isolated (after threefold recrystallization of the initially formed mixture of isomers **3a,b** from the methanol—ether system) in the stereochemically individual state (>98% *de*) in 44% yield (with respect to Pd).

It should be noted that when the resolution of racemic stilbenediamine was conducted with the use of the starting ratio Pd : Stien = 1 : 2, we failed to obtain diamine adduct **3a** in the analytically pure form. According to the data of elemental analysis and ^{1}H NMR spectroscopy (see Experimental), samples of the complex isolated at all stages of resolution contained an additional (nonstoichiometric) amount of free diamine Stien, which was tightly held by the complex and could not be removed by extraction, recrystallization, or chromatographic methods. Its presence was confirmed by ^{1}H NMR spectroscopy. The spectra of the complex reveal a signal from the C(α)H protons of the free Stien molecule as a singlet at δ 3.96 in methanol-d_4 and acetonitrile-d_3 or at δ 3.870 in DMSO-d_6 (at δ 3.873 in the spectrum of free diamine measured in DMSO-d_6). The identity of the (*SS*) absolute configuration both of the free and chelated diamine Stien molecules in the (S_CR_N,*SS*)-**3a** · *n*(*SS*)-Stien adducts is confirmed by the fact that the ^{1}H NMR spectra have no signals corresponding to the second diastereomer (S_CR_N,*RR*)-**3b**, which appeared previously due to exchange when free diamine with the opposite configuration is added.

Subsequent X-ray diffraction analysis of less soluble diastereomer (S_CR_N,*SS*)-**3a** confirmed that it crystallized as an associate with an additional diamine molecule of the same configuration. The stoichiometry was Pd : Stien = 2 : 3 (see below). The idea of the practical use of this peculiar double (inner- and outer-sphere) selection in the course of optical resolution of diamine seems to be a rather attractive one.

In this connection, we carried out subsequent experiments (method ***C***, see Experimental) with the use of a sixfold excess of racemic diamine in the reaction with dimer (S_CR_N)-**2** (Pd : Stien = 1 : 3) and using MeCN as the solvent, which appeared to be optimum for crystallization of this associate. After slow double recrystallization of a mixture of diastereomers **3a,b** from MeCN, the individual diastereomer of the dimeric associate (S_CR_N,*SS*)-**3a** · 0.5Stien (**4**) was isolated in the analytically pure form in satisfactory yield (66% with respect to Pd and diamine) with high optical purity (>98% *de*).

After resolution, diamine Stien was isolated from complex **4** in high yield (85%) by simple protonation with dilute HCl in the two-phase CH_2Cl_2—H_2O system. In this case, we succeeded in regenerating the initial resolving agent in almost quantitative yield (98%) as dimer (S_CR_N)-**2** suitable for reuse. The value of the specific rotation of free stilbenediamine ($[\alpha]_D$ −106.2°, *cf.* Ref. 42) confirms its high enantiomeric purity (~99% *ee*) and the sign of rotation allows the assignment of the (*SS*) absolute configuration to the enantiomer of Stien isolated.[43,44]

Structure of complex (S_CR_N,SS)-3a in solution

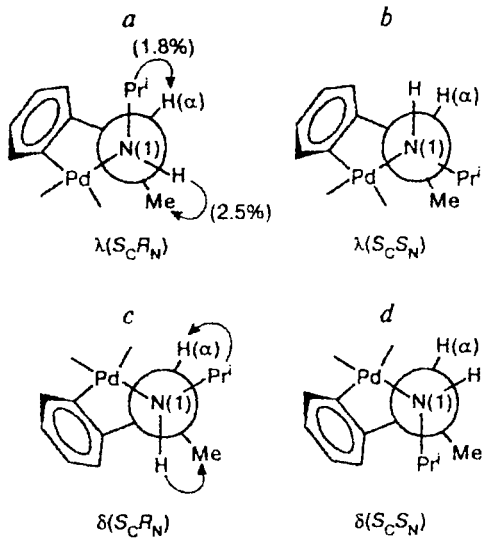
The structure and stereochemical purity of diastereomer (S_CR_N,*SS*)-**3a** were confirmed by high-resolution ^{1}H NMR spectra measured in three solvents, namely, in acetonitrile-d_3 and DMSO-d_6 (which give complete spectral patterns) as well as in methanol-d_4 (it allows one to simplify the spectra due to NH/ND exchange, which leads to the disappearance of signals of the NH group and to elimination of the spin-spin interaction with them). The assignment of the signals was made based on the double homonuclear resonance and on the experiments with the use of the nuclear Overhauser effect (NOE). Under all conditions, the ^{1}H NMR spectra of samples of adduct (S_CR_N,*SS*)-**3a** isolated according to methods ***B*** and ***C*** have only one set of signals, which correspond to one of two diastereomers. This confirms its high optical purity (>98% *de*). The diastereomeric purity of complex (S_CR_N,*SS*)-**3a** prepared according to method ***A*** (88% *de*) was determined by integration of the signals from the protons of the *N*-isopropyl substituent in the palladacycle using simulation of spectral lines.

The absence of diastereoselectivity upon complexation of dimer (S_CR_N)-**2** with racemic diamine Stien in a solution called for corroboration of the fact that the stereochemistry of the palladacycle, which was established by X-ray diffraction analysis of the complex in the crystalline state, is retained in solutions. Without considering the polarity of the medium, it can be suggested that diamine adduct **3a** should retain the (S_CR_N) stereochemistry of the starting dimer typical of N*-chiral palladacycles.[41,45,46] The same conclusion follows from the analysis of the Newman projections along the N(1)—C(α) bond for the two absolute configurations of the nitrogen atom (R_N and S_N) in the case of the λ and δ conformations of the palladacycle.

Scheme 2 shows the Newman projections of the (S_C)-*N*-Pr^i-benzylaminate palladacycle along the

N(1)—C(α) bond in the case of the (R_N) (*a* and *c*) and (S_N) configurations (*b* and *d*) of the asymmetric nitrogen atom for the λ (*a* and *b*) and δ conformations (*c* and *d*) of the five-membered metallacycle. The projections were constructed taking into account the actual dihedral angles determined by X-ray diffraction analysis of complex **3a**. The closely-spaced (according to the NOE data) protons are indicated by arrows.

Scheme 2



A comparison of two pairs of the projections demonstrates that in both conformations (λ and δ) of the palladacycle the occurrence of the alternative (S_CS_N) configuration of the nitrogen atom is associated with the unfavorable arrangement of the bulky Pr^i substituent at the nitrogen atom in proximity to the α-Me group. Due to flattening of the palladacycle, these groups are forced to be in an almost mutually eclipsed arrangement with the dihedral angle of 16—19° (see Scheme 2, *b* and *d*).

The NOE experiments, which were carried out in DMSO-d_6 at 40 °C (at this temperature, the best resolution of signals from the protons of the amino groups was obtained) provided direct evidence for the retention of the (S_CR_N) stereochemistry of the palladacycle in solutions of the diastereomer of ionic complex **3a** under study. Irradiation of the N(1)H proton of the palladacycle (δ 6.051) resulted in NOE for the protons of the α-Me group (δ 1.693, 2.5%), while irradiation of the protons of the Me groups of the *N*-isopropyl substituent (δ 1.25) led to NOE for the α-methine proton of the palladacycle (δ 4.119, 1.8%). Since these effects can occur only if the interacting protons are in rather close proximity (see Scheme 2, *a* and *c*), the (S_CR_N) configuration is admittedly the only configuration of the palladacycle in which both effects can occur simultaneously.

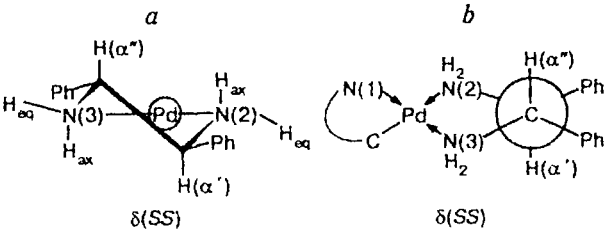
A choice between the possible conformations (λ and δ) of the (S_CR_N)-palladacycle can be made based on the analysis of the efficiency of the spin-spin interaction between the C(α)H and N(1)H protons. From the comparison of two Newman projections (see Scheme 2, *a* and *c*), it is evident that in the case of the λ conformation these two bonds are virtually orthogonal to each other, while in the case of the δ conformation they are in the mutually quasi-transoid arrangement (the H—C(α)—N(1)—H torsion angles are −100° and ~135°, respectively). Consequently, according to Karplus—Conroy's equation,[47] significant values of the spin-spin coupling constant $^3J_{HC(\alpha)-NH}$ can be expected only for the δ conformation of the (S_CR_N)-palladacycle. In the ^{1}H NMR spectrum of adduct (S_CR_N,*SS*)-**3a** (measured in acetonitrile-d_3), the α-methine proton gives a quartet (at δ 4.100, $^3J_{HH}$ = 6.6 Hz) due to its interaction with the α-Me group. The N(1)H proton gives a broadened doublet (at δ 6.270, $^3J_{HN-CH}$ = 5.5 Hz). The double resonance unambiguously confirms that this proton is split only on the methine proton of the *N*-isopropyl substituent. Therefore, the C(α)H and N(1)H protons virtually do not interact, which allows one to conclude with a fair degree of assurance that the contribution of the δ conformation of the (S_CR_N)-palladacycle (see Scheme 2, *c*) to the conformational equilibrium of this system is negligible. This argument also allows one to exclude both (λ and δ) conformations of the (S_CS_N)-palladacycle (see Scheme 2, *b* and *d*) from consideration because in the case of this stereochemistry the dihedral angle should be smaller than 20° and the constant $^3J_{HC(\alpha)-NH}$ should have a rather large observed value.[47] Therefore, only the λ(S_CR_N) stereochemistry of the palladacycle agrees with the spectral data on ionic complex **3a** in a solution.

The essential difference between the structure of the *N*-isopropyl-α-methylbenzylaminate palladacycle involved in cationic complex (S_CR_N,*SS*)-**3a** and the structures of the neutral adducts studied previously[38,45,46] is in the virtually complete rotameric lability of the *N*-Pr^i group in the first case. This is primarily manifested in the extremely low diastereotopic nonequivalence of the two Me groups of this substituent whose chemical shifts differ by no more than 0.03 ppm (*cf.* the corresponding values for the pyridine adducts of the same palladacycle[38] and its *N*-Me-substituted analog;[45] Δδ = 0.21 and 0.89, respectively). The rotameric lability of the *N*-Pr^i substituent is additionally confirmed by NOE observed for both Me groups (2.6%) as well as for the methine proton (1.5%) of the $CHMe_2$ substituent under irradiation of the N(1)H proton of the palladacycle. Apparently, this lability is associated with the use of highly polar solvents capable of being coordinated. These solvents efficiently compete for the axial coordination vacancies at the metal atom and rupture weak agostic (Pr^i)H···Pd interactions, which generally increase the barrier to rotation of the *N*-isopropyl group in neutral complexes with the same[41] or analogous palladacycles.[39,40] The existence of

solvation is indirectly supported by the fact that in some experiments, NOE (up to 1.2%) was observed for the residual protons of DMSO under preirradiation of the protons of the palladacycle.

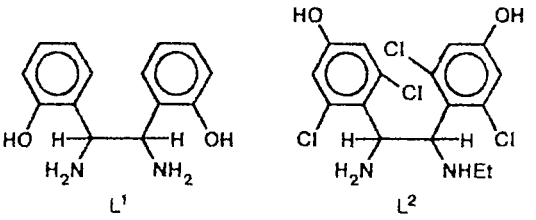
The positions and multiplicities of the signals from the NH protons of the two primary amino groups of stilbenediamine (two broadened doublets and two doublets of doublets, which take the form of a quasi-triplet) as well as their diastereotopic nonequivalence confirm the bidentate coordination of the diamine to the palladium(II) atom in a solution; in DMSO-d_6, the coordination shifts $\Delta\delta$ = 1.9—3.5. According to the accepted concept of the strong preference of the equatorial orientation of *C*-substituents in five-membered diamine metallacycles,[17,35,36,48] which is based on the data of ^{1}H and ^{13}C NMR spectra in solutions and on the X-ray diffraction data for the solid state, it can be *a priori* suggested that (*SS*)-Stien included into diastereomer **3a** should exist predominantly in the δ conformation with both Ph groups in equatorial positions and the methine protons in axial orientations. The preferred conformation of the five-membered metallacycle formed by (*SS*)-stilbenediamine (*a*) and the Newman projection along the C—C bond between two benzyl stereocenters for this conformation (*b*) are shown in Scheme 3.

Scheme 3



This δ conformation of the diamine metallacycle in complex (S_CR_N,*SS*)-**3a** is strongly supported by the large value (11.6 Hz) of the constant $^3J_{HH}$ for two axial benzyl H(α') and H(α") protons of diamine (δ 4.251 and 4.302, respectively; AB system) in the ^{1}H NMR spectrum measured in methanol-d_4. This fact is indicative of their mutually transoid arrangement. These methine protons become chemically nonequivalent because Stien loses the initial symmetry C_2 upon coordination with the unsymmetrical *C,N*-palladacycle.

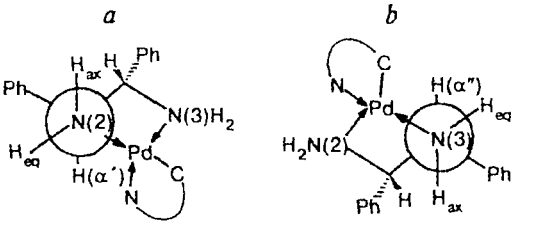
For comparison, it should be noted that quite similar values of $^3J_{HH}$ have been observed previously for the methine protons in the (*RR*) and (*SS*) enantiomers of diamine Me_4bn in the ^{1}H NMR spectra of their adducts with *ortho*-palladated dimer (*S*)-**1c** (11.2 and 11.5 Hz, respectively).[17] Analogous values of $^3J_{HH}$ were also reported for simple coordination complexes of platinum(II) with Ph- and *N*-substituted derivatives of stilbenediamine: $^3J_{HH}$ = 12.4 Hz for the unsymmetrical complex [{(*S,S*)-L^1}Pt(DMSO)SO$_4$] containing the symmetrical ligand L^1 [35] and $^3J_{HH}$ = 12.1 Hz for the symmetrical complex [L^{2}PtCl$_2$] containing the *threo* diastereomer of the unsymmetrically *N*-substituted analog of diamine Stien L^2.[36]



Such characteristics are generally interpreted as an indication of the large value of the H—C—C—H dihedral angle (*ca.* 180°) between the two methine protons in the diamine metallacycles with the δ(*SS*) or λ(*RR*) stereochemistry.[17,35,36]

The elucidation of the δ conformation of the (*S,S*)-diamine metallacycle allows the assignment of the signals of the diastereotopic NH groups of the coordinated Stien ligand. The Newman projections along the N(2)—C(α) (*a*) and N(3)—C(α) (*b*) bonds in the diamine metallacycle in the case of its δ(*S,S*) stereochemistry are shown in Scheme 4. It can be seen that the dihedral angles between the methine C(α)—H bond and the two nearest NH groups in the halves of the diamine molecule are substantially different. In the crystal of (S_CR_N,*SS*)-**3a**, these angles are −48° and −40° for two equatorial NH protons, while they are 168° and 157° (the supplementary angles are 12° and 23°, respectively) for the axial protons of the N(2)H$_2$ and N(3)H$_2$ groups, respectively. It is reasonable to expect that this difference should be reflected in the efficiency of their spin-spin interactions with α-methine protons.

Scheme 4

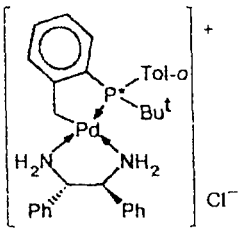


According to this suggestion, the quasi-triplet signals at δ 4.055 and 2.822 in the ^{1}H NMR spectrum of complex (S_CR_N,*SS*)-**3a** (measured in acetonitrile-d_3) are characterized by rather large values of the constant $^3J_{HN-CH}$ (10.5 and 10.0 Hz, respectively). This indicates that the dihedral angles between the NH and CH bonds are close to 180° and, consequently, these two signals can be assigned to the protons of the axial N(2)H$_{ax}$ and N(3)H$_{ax}$ groups. Since there is no evidence of splitting at the nearest α-methine proton for the two

remaining doublet signals at δ 4.518 and 5.85 (the geminal constants $^2J_{HNH}$ are 10.3 and 10.9 Hz, respectively), these signals can be assigned to the equatorial $N(2)H_{eq}$ and $N(3)H_{eq}$ groups of the chelated diamine Stien molecule.

The differentiation of the two primary amino groups of the diamine ligand ($N(2)H_2$ and $N(3)H_2$) was made based on NOE (1.4%) observed for the C(6)H proton (nearest to the palladation site) of the aromatic ring of the benzylaminate ligand (doublet at δ 7.04 in DMSO-d_6) under irradiation at the frequency of the most low-field doublet signal (δ 5.524 in DMSO-d_6) of the equatorial amino groups of diamine Stien. Of all the hydrogen atoms of the amino groups of diamine, only the equatorial proton belonging to the primary amino group, which is in the *trans* position with respect to the donor nitrogen atom of the palladacycle ($N(3)H_{eq}$), can be located in proximity to the aromatic C(6)H proton. For comparison, in the crystal of **3a** the distance between these protons, N(3)H(3a)···H(2b)C(2), is 2.361 Å. The validity of the assignment made can be additionally supported by the fact that this proton gives the most low-field signal, which is due to the deshielding influence of the aromatic ring of the *ortho*-palladated benzylamine ligand. This provides the basis for the subsequent identification of the signals from the remaining protons of the amino groups based on the results of the double homonuclear resonance.

To our knowledge, diastereomer (S_CR_N,*SS*)-**3a** is the first example of an adduct of stilbenediamine with an *ortho*-palladated complex, which was characterized by spectral and structural methods (see below). Only one example of the synthesis of the (−)-Stien cyclometallated derivative (without detailed spectral characterization) has been reported to date. It is diamine adduct **5** of cyclopalladated phosphine prepared in an attempt to achieve optical resolution of the P*-chiral palladacycle, which was unsuccessful.[49]



(S_P/R_P,*SS*)-**5**

To confirm the absolute configuration of stilbenediamine (both of the Pd-chelated Stien and that of solvation) incorporated into the complex and to reveal the driving force for its cocrystallization with an additional molecule of diamine, we carried out X-ray diffraction study of less soluble diastereomer (S_CR_N,*SS*)-**3a**.

Structure of diastereomer (S_CR_N,SS)-3a in the crystalline state

A crystal suitable for X-ray diffraction study was prepared by recrystallization of individual diastereomer **3a** (isolated under conditions of method *B*) from acetonitrile in the presence of methanol traces. The structure of the complex is shown in Figs. 1 and 2. The bond lengths and bond angles are given in Tables 1 and 2, respectively. The absolute stereochemistry of the complex was established, including the λ(S_CR_N) configuration of the palladacycle and the δ(*S*,*S*) configuration of the diamine Stien ligand.

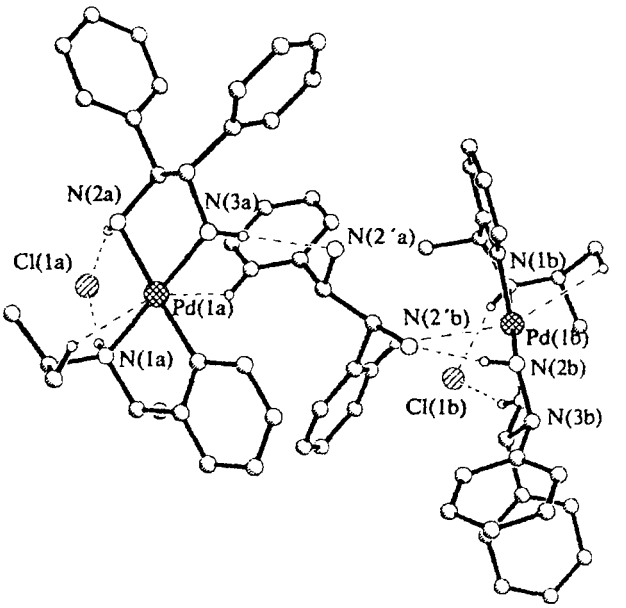


Fig. 1. Molecular structure of the dimeric associate (**4**) of adduct (S_CR_N,*SS*)-**3a** with an additional bridging diamine (*SS*)-Stien molecule (the "a" and "b" letters correspond to two symmetrical halves of the associate related by a twofold axis).

The most unusual structural feature of the complex is that it exists as C_2-symmetric dimer **4** containing an additional molecule of diamine Stien as a bridge between two mononuclear complex cations **3a** (see Fig. 1). Association occurs *via* the N(3)—H···N(2′) hydrogen bonds between the amino groups of the chelated stilbenediamine molecule and the nitrogen atoms of the bridging stilbenediamine molecule. The H···N distance is 2.281 Å. It can be assumed that the associate can be additionally stabilized through a weak agostic interaction between one of the *ortho*-protons of the Ph ring of the bridging Stien molecule and the palladium atom. The H···Pd distance is 3.05 Å. It should be noted that this proton is located almost exactly above the metal atom. The angle between the agostic H···Pd bond and the normal to the mean coordination plane is 2.2°.

In the mononuclear complex cation of adduct (S_CR_N,*SS*)-**3a**, the coordination environment about the Pd atom is a virtually regular planar square. The deviations of the atoms bonded to the Pd atom from the mean coordination plane {$PdCN_3$} are no more than ±0.05 Å. The angle between the {Pd(1)N(1)C(1)} and {Pd(1)N(2)N(3)} planes is 4.6°; however, the distortion is not tetrahedral in character (see Fig. 2).

The benzylaminate palladacycle adopts a nearly classical envelope-like conformation. The nitrogen atom

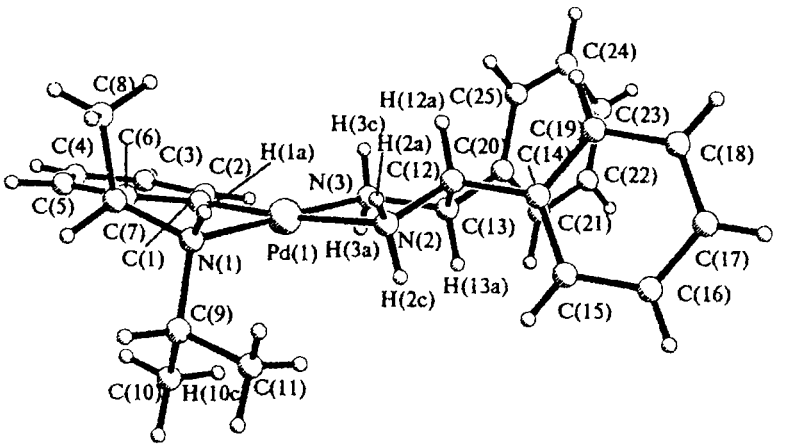


Fig. 2. Projection of the complex cation (S_CR_N,*SS*)-**3a** onto the plane, which is approximately orthogonal to the mean coordination plane; the projection illustrates the conformational features of the palladacycle and the diamine chelate ring.

deviates from the plane through the remaining four atoms by −0.445 Å. The folding angle along the Pd(1)···C(7) line is 26.6°. It should be noted that the average value of the intrachelate dihedral angles is only 16.0° compared to 19.8—22.3° in the case of the starting dimeric complex (S_CR_N)-**2** [41] and 27° for the sterically more hindered α-Bu^t-substituted analog,[50] which indicates that the palladacycle is flattened to some extent.

According to the above-considered results of analysis of the ^{1}H NMR spectra, the asymmetric donor nitrogen atom in the palladacycle retains the (R_N) absolute configuration of the starting dimer (S_CR_N)-**2**, whose stereochemistry has been established previously by X-ray diffraction analysis.[41] As in the case of the starting dimer (S_CR_N)-**2**, the bulky *N*-isopropyl substituent in ionic complex (S_CR_N,*SS*)-**3a** is in the quasi-transoid position with respect to the α-Me group at the C* stereocenter. The N—C(9) (Pr^i) and C(7)—C(8) (α-Me) bonds form angles of 28.0° and 165.7° (the supplementary angle is 14.3°), respectively, with the normal to the mean coordination plane (see Fig. 2).

Unlike solutions, in the crystal of complex **3a** the quasi-axial orientation of the *N*-Pr^i group is to some extent stabilized by the agostic interaction between one of the protons of its Me group and the palladium atom. The Pd(1)···H(10c) distance (2.858 Å) is close to those determined previously for the starting dimer (S_CR_N)-**2** (2.84—2.92 Å)[41] and is substantially smaller than the sum of the van der Waals radii of these atoms (3.1 Å).[51]

As one would expect, the diamine metallacycle is considerably more twisted than the palladacycle (the average intrachelate torsion angle is 32.2°) and adopts an asymmetrical twist conformation. Its stereochemistry is consistent with that expected for coordinated 1,2-diamines with the (*S*,*S*) absolute configuration.[35,52] The (*S*,*S*)-Stien ligand in the complex cation is fixed in the δ conformation with both C—Ph fragments in virtually equatorial positions: the C(12)—C(14) and C(13)—C(20) bonds between the carbon atoms of the ethylene bridge and the *ipso*-C atoms of the Ph groups are located virtually in the mean coordination plane: the angles with the normal to this plane are 83.2° and 107.7°, respectively.

Table 1. Bond lengths (*d*) in the (S_CR_N,*SS*)-**3a** · 0.5(*SS*)-Stien complex

Bond	*d*/Å	Bond	*d*/Å	Bond	*d*/Å
Pd(1)—C(1)	1.973(5)	C(6)—C(7)	1.487(7)	C(20)—C(21)	1.383(7)
Pd(1)—N(3)	2.058(4)	C(7)—C(8)	1.509(7)	C(21)—C(22)	1.387(8)
Pd(1)—N(1)	2.076(4)	C(9)—C(11)	1.517(7)	C(22)—C(23)	1.336(10)
Pd(1)—N(2)	2.152(4)	C(9)—C(10)	1.526(8)	C(23)—C(24)	1.365(11)
N(1)—C(9)	1.494(6)	C(12)—C(14)	1.527(7)	C(24)—C(25)	1.396(8)
N(1)—C(7)	1.505(6)	C(12)—C(13)	1.564(7)	N(2')—C(7')	1.460(8)
N(2)—C(12)	1.479(6)	C(13)—C(20)	1.500(7)	C(1')—C(2')	1.361(9)
N(3)—C(13)	1.499(6)	C(14)—C(15)	1.374(7)	C(1')—C(6')	1.393(8)
C(1)—C(6)	1.398(7)	C(14)—C(19)	1.390(8)	C(1')—C(7')	1.525(9)
C(1)—C(2)	1.400(7)	C(15)—C(16)	1.399(7)	C(2')—C(3')	1.385(13)
C(2)—C(3)	1.381(8)	C(16)—C(17)	1.348(10)	C(3')—C(4')	1.41(2)
C(3)—C(4)	1.376(8)	C(17)—C(18)	1.353(10)	C(4')—C(5')	1.34(2)
C(4)—C(5)	1.383(9)	C(18)—C(19)	1.392(9)	C(5')—C(6')	1.339(11)
C(5)—C(6)	1.401(7)	C(20)—C(25)	1.374(8)	C(7')—C(7')	1.523(11)

Table 2. Bond angles (ω) in the (S_CR_N,*SS*)-**3a** · 0.5(*SS*)-Stien complex

Angle	ω/deg	Angle	ω/deg	Angle	ω/deg
C(1)—Pd(1)—N(3)	96.8(2)	C(5)—C(6)—C(7)	121.2(5)	C(18)—C(19)—C(14)	119.5(7)
C(1)—Pd(1)—N(1)	82.6(2)	C(6)—C(7)—N(1)	108.3(4)	C(25)—C(20)—C(21)	117.4(5)
N(3)—Pd(1)—N(1)	179.2(2)	C(6)—C(7)—C(8)	112.1(4)	C(25)—C(20)—C(13)	122.9(5)
C(1)—Pd(1)—N(2)	175.4(2)	N(1)—C(7)—C(8)	109.3(4)	C(21)—C(20)—C(13)	119.6(5)
N(3)—Pd(1)—N(2)	81.9(2)	N(1)—C(9)—C(11)	110.9(4)	C(20)—C(21)—C(22)	120.9(6)
N(1)—Pd(1)—N(2)	98.6(2)	N(1)—C(9)—C(10)	110.7(4)	C(23)—C(22)—C(21)	120.5(6)
C(9)—N(1)—C(7)	111.8(4)	C(11)—C(9)—C(10)	111.1(5)	C(22)—C(23)—C(24)	120.7(6)
C(9)—N(1)—Pd(1)	115.3(3)	N(2)—C(12)—C(14)	114.2(4)	C(23)—C(24)—C(25)	119.2(7)
C(7)—N(1)—Pd(1)	110.0(3)	N(2)—C(12)—C(13)	107.0(4)	C(20)—C(25)—C(24)	121.3(6)
C(12)—N(2)—Pd(1)	107.8(3)	C(14)—C(12)—C(13)	110.3(4)	C(2′)—C(1′)—C(6′)	118.5(7)
C(13)—N(3)—Pd(1)	112.0(3)	N(3)—C(13)—C(20)	111.8(4)	C(2′)—C(1′)—C(7′)	121.6(6)
C(6)—C(1)—C(2)	117.7(5)	N(3)—C(13)—C(12)	108.0(4)	C(6′)—C(1′)—C(7′)	119.9(6)
C(6)—C(1)—Pd(1)	113.8(4)	C(20)—C(13)—C(12)	113.6(4)	C(1′)—C(2′)—C(3′)	121.6(8)
C(2)—C(1)—Pd(1)	128.4(4)	C(15)—C(14)—C(19)	118.7(5)	C(2′)—C(3′)—C(4′)	117.1(9)
C(3)—C(2)—C(1)	121.7(5)	C(15)—C(14)—C(12)	121.6(5)	C(5′)—C(4′)—C(3′)	120.9(9)
C(4)—C(3)—C(2)	120.2(5)	C(19)—C(14)—C(12)	119.7(5)	C(6′)—C(5′)—C(4′)	121.1(9)
C(3)—C(4)—C(5)	119.4(5)	C(14)—C(15)—C(16)	120.3(6)	C(5′)—C(6′)—C(1′)	120.8(8)
C(4)—C(5)—C(6)	120.8(5)	C(17)—C(16)—C(15)	120.2(7)	N(2′)—C(7′)—C(1′)	109.6(5)
C(1)—C(6)—C(5)	120.0(5)	C(16)—C(17)—C(18)	120.3(6)	N(2′)—C(7′)—C(7′)	113.6(4)
C(1)—C(6)—C(7)	118.7(4)	C(17)—C(18)—C(19)	120.9(7)	C(1′)—C(7′)—C(7′)	110.6(4)

The mutual orientation of these bonds is close to the ideal *gauche* arrangement: the C(20)—C(13)—C(12)—C(14) torsion angle is −58.3°. This value is intermediate between the values of the corresponding dihedral angle in two independent molecules of the complex [{(−)-L^1}$PtCl_2$] (**6**) (−56.8° and −59.1°) reported previously.[35] The intrachelate N(2)—C(12)—C(13)—N(3) torsion angle in complex **3a** is somewhat smaller (52.4°) than those in two molecules of complex **6** (53.9° and 58.1°).[35]

According to this conformation, the two methine C—H bonds of the diamine are in the ideal mutually transoid arrangement (see Fig. 2): the H(12a)—C(12)—C(13)—H(13a) torsion angle is 179.6°. Both these C—H bonds are in axial positions with respect to the mean coordination plane: the angles with the normal to this plane are 167.3° (the supplementary angle is 12.7°) and 13.5°. This agrees well with the data of ^{1}H NMR spectroscopy for complex **3a** in solutions.

It is conceivable that the system of hydrogen bonds involving the secondary and primary amino groups is one of the causes of asymmetry of the diamine chelate ring and of some anomalies in the structure of the palladacycle. In addition to the above-mentioned intermolecular hydrogen bonds between the chelated and bridging stilbenediamine ligands, intramolecular N—H···Cl hydrogen bonds are detected in the structure of complex **3a**. Each Cl^- anion is involved in two such bonds with the equatorial NH groups of the benzylaminate palladacycle and of the chelated stilbenediamine ligand of the same complex cation, which leads to the formation of a six-membered quasi-chelate hydrogen-bonded ring. These hydrogen bonds, which are oriented at the H(1a)···Cl(1)···H(2a) angle of 68.4°, belong to rather strong bonds: the Cl(1)···H(1a) and Cl(1)···H(2a) distances (2.477 and 2.447 Å, respectively) are considerably smaller than the sum of the van der Waals radii of these atoms (3.0 Å).[51]

The molecule of the outer-sphere bridging stilbenediamine molecule has the same (*S*,*S*) absolute configuration and the δ conformation as those found for the palladium-chelated diamine molecule. The geometric parameters of the former differ only slightly from those observed for the diamine molecule incorporated into the complex cation. Thus, the Ph—C—C—Ph, N—C—C—N, and H—C(α)—C(α)—H torsion angles in the bridging Stien molecule are −67.8°, 44.7°, and 166.7°, respectively. These values are close to the corresponding parameters of the chelated diamine molecule (−58.3°, 52.4°, and 179.6°, respectively) as well as to the characteristics of (*R*,*R*)-Stien monohydrobromide (64.3°, −44.3°, and −173.5°, respectively)[44] taking into account the opposite absolute configuration of this salt.

It should be noted that the above-considered dimeric associate of diamine complex (S_CR_N,*SS*)-**3a** provides the first example of the outer-sphere bridged coordination of stilbenediamine.

* * *

We believed that from the practical standpoint the most important result of X-ray diffraction analysis of adduct (S_CR_N,*SS*)-**3a** is the fact that two homochiral palladacycles can bind three diamine molecules with the same (*SS*) absolute configuration. This demonstrates the possibility of the double (not only intra-sphere but also outer-sphere) selection of enantiomers of diamine in the course of selective crystallization of its adducts with the *ortho*-palladated matrix.

To our knowledge, this is the first example of such unusual stoichiometry, which seems to be very economically attractive. In the majority of the presently

known procedures for the optical resolution of bidentate ligands with the use of *ortho*-palladated matrices, the standard stoichiometry (palladacycle : substrate = 1 : 1) is observed in diastereomers isolated.[1,13,14,16,53] Moreover, in some instances (for example, in the case of resolution of bidentate phosphino- and arsinothiolates[11,12,54] and bulky bidentate *N*-donor ligands[8,55,56]) the situation becomes even less favorable. The consumption of the rather expensive Pd-containing reagent is doubled due to the bridged coordination of one molecule of the substrate being resolved with two palladacycles. Therefore, the palladium : ligand ratio increases to 2 : 1.

In principle, alternative procedures for the preparation of enantiomerically pure diamine Stien, namely, by resolving the racemate by recrystallization of its salt with tartaric[57–59] or mandelic acid[42,60] or by asymmetric synthesis,[61–63] are known. However, asymmetric syntheses are generally rather tedious multistage procedures that afford optically active diamine in small final yields. Resolution *via* salt formation with tartaric acid requires multiple recrystallization, which also leads to a decrease in the yield.

The procedure for the preparation of optically active stilbenediamine proposed by us has certain advantages over the known procedures. First, it is a simple one-stage resolution procedure the course of which can be directly monitored by ^{1}H NMR spectroscopy. Besides, the dimeric *ortho*-palladated complex (S_CR_N)-**2** may be regenerated in almost quantitative yield, which allows one to solve the problem of high cost of the resolving reagent. This reagent can be readily prepared from commercially available (*S*)-α-methylenebenzylamine.[38] Well-developed procedures for the diastereoselective synthesis of racemic stilbenediamine[42,57,61,64,65] and its Ph-substituted derivatives,[59] which are free of the *meso* form, substantially facilitate the realization of this approach.

The versatility of the reagents of this class is an additional advantage of resolution with the use of optically active *ortho*-palladated matrices, such as dimer (S_CR_N)-**2**. These reagents are suitable for resolving virtually all substrates, which are able to be coordinated to palladium. Possibly, the further development of this promising field of practical stereochemistry will bring us closer to the creation of a universal tool for the optical resolution of any substrate possessing ligand properties.

Experimental

The ^{1}H NMR spectra were recorded on a Varian VXR-400 spectrometer (400 MHz) in $CDCl_3$, methanol-d_4, acetonitrile-d_3, or DMSO-d_6. Chemical shifts were measured relative to signals of residual protons of deuterated solvents (Me_4Si as the internal standard; δ scale). The assignment of the signals was made with the use of the double homonuclear resonance and the Overhauser effect. The specific rotation at the wavelength of the sodium *D* line was measured on an automated A1-EPO polarimeter (VNIEKIProdmash). The solvents were purified according to standard procedures.

Di-μ-chlorobis{(S_CR_N)-2-[1-(*N*-isopropylamino)ethyl]-phenyl-*C*,*N*}dipalladium(II) ((S_CR_N)-2) was synthesized according to a known procedure.[38]

Racemic 1,2-diphenylethane-1,2-diamine (Stien) was prepared according to a known procedure[64,65]; m.p. 81—83 °C (published data: m.p. 80—82 °C [64,65]); R_f 0.43 (Silufol, MeOH—Et_3N, 50 : 1). ^{1}H NMR ($CDCl_3$), δ: 1.612 (br.s, 4 H, NH_2); 4.111 (s, 2 H, C(α)H); 7.282 (s, 10 H, Ph). ^{1}H NMR (DMSO-d_6), δ: 2.05 (br.s, 4 H, NH_2); 3.873 (s, 2 H, C(α)H); 7.1—7.2 (m, 10 H, Ph).

Stereochemistry of dimer (S_C,R_N)-2 complexation with racemic stilbenediamine. A solution of a mixture of dimer (S_C,R_N)-**2** with (*RR*,*SS*)-Stien taken in a diamine : palladium ratio of 2 : 1 in methanol-d_4 was prepared. The ^{1}H NMR spectrum measured at ~20 °C contains two sets of signals of diastereomeric complexes **3a,b** in a ratio of ~1 : 1 along with signals of an excess of free diamine (signals from the protons of the amino groups are not observed due to H/D exchange). ^{1}H NMR (methanol-d_4), δ, (S_CR_N,*SS*)-**3a**: 1.265 (d, 3 H, CH$\underline{Me}_2$, $^3J_{HH}$ = 6.4 Hz); 1.293 (d, 3 H, CH$\underline{Me}_2$, $^3J_{HH}$ = 6.5 Hz); 1.725 (d, 3 H, α-Me, $^3J_{HH}$ = 6.7 Hz); 3.066 (m, 1 H, C$\underline{H}$Me$_2$); 4.128 (q, 1 H, C(α)H of the palladacycle, $^3J_{HH}$ = 6.4 Hz); 4.302 and 4.259 (AB system, 2 H, C(α)H, Stien, $^3J_{AB}$ = 11.7 Hz); 6.80—7.33 (m, 14 H, H arom.); (S_CR_N,*RR*)-**3b**: 1.271 (d, 3 H, CH$\underline{Me}_2$, $^3J_{HH}$ = 6.4 Hz); 1.384 (d, 3 H, CH$\underline{Me}_2$, $^3J_{HH}$ = 6.4 Hz); 1.740 (d, 3 H, α-Me, $^3J_{HH}$ = 6.4 Hz); 3.066 (m, 1 H, C$\underline{H}$Me$_2$); 4.112 (q, 1 H, C(α)H of the palladacycle, $^3J_{HH}$ = 6.4 Hz); 4.226 and 4.116 (AB system, 2 H, C(α)H, Stien, $^3J_{AB}$ = 11.4 Hz); 6.80—7.33 (m, 14 H, H arom.); free Stien: 3.95 (s, 2 H, C(α)H); 7.12 (s, 10 H, Ph).

{(S_CR_N)-2-[1-(*N*-Isopropylamino)ethyl]phenyl-*C*,*N*}{(*SS*)-1,2-diphenyl-1,2-ethanediamine-*N*,*N*'}palladium(II) chloride ((S_CR_N,*SS*)-3a). *A* (Pd : Stien = 1 : 1). Two equivalents of racemic stilbenediamine (0.411 g, 1.938 mmol) were added to a suspension of dimer (S_CR_N)-**2** (0.589 g, 0.969 mmol) in anhydrous MeOH (10 mL). After stirring under argon for 40 min, the reaction mixture was filtered, concentrated on a rotary evaporator to the oily state, and dissolved in dry MeCN (7 mL). The reaction mixture was allowed to slowly crystallize in the cold. After 2 days, the colorless crystalline complex (0.390 g) was filtered off. Repeated slow recrystallization from dry MeCN containing traces of MeOH and drying *in vacuo* (1 Torr) over $CaCl_2$ and paraffin allowed the isolation of less soluble diastereomer (S_CR_N,*SS*)-**3a** in the crystalline state as a monohydrate (we failed to remove the H_2O molecule even upon prolonged evacuation at 10^{-2} Torr) in 51% yield (0.262 mg, 0.490 mmol), m.p. 204—206 °C (decomp.), $[\alpha]_D^{20}$ −34.3° (*c* 1.5, MeOH) and the optical purity was 88% *de* (determined by integration of the signals from the protons of the Me groups of the Pr^i substituent). Found (%): C, 56.01; H, 6.14; N, 7.75. $C_{25}H_{32}ClN_3Pd \cdot H_2O$. Calculated (%): C, 56.18; H, 6.41; N, 7.86.

B (Pd : Stien = 1 : 2). A fourfold molar excess of racemic stilbenediamine (0.797 g, 3.755 mmol) was added with stirring to a suspension of dimer (S_CR_N)-**2** (0.571 g, 0.939 mmol) in anhydrous MeOH (10 mL). After the reaction mixture was stirred under argon for 40 min, it was filtered and concentrated to 2—3 mL. Anhydrous ether was slowly added. The colorless finely crystalline precipitate that formed was filtered off and doubly recrystallized from a minimum amount of anhydrous MeOH by slow addition of anhydrous ether followed by cooling. After drying *in vacuo* (1 Torr) over $CaCl_2$ and paraffin, individual diastereomer (S_CR_N,*SS*)-**3a** was obtained in a yield of 44% with respect to Pd and 57% with respect to diamine (0.478 g, 0.824 mmol) as an associate containing 0.3 diamine (*SS*)-Stien molecule of solvation; m.p. 205 °C

Table 3. Principal characteristics of X-ray diffraction study of (S_CR_N,*SS*)-**3a** · 0.5(*SS*)-Stien

Parameter	Data and conditions of X-ray study
Molecular formula	$C_{32}H_{40}ClN_4Pd$
Molecular weight	622.6
Color	Light-yellow
Crystal dimensions/mm	0.12×0.18×0.30
System	Orthorhombic
Space group	$P2_12_12$
Unit cell parameters:	
a/Å	15.350(4)
b/Å	23.348(9)
c/Å	8.396(1)
α/deg	90
β/deg	90
γ/deg	90
V/Å^3	3009.1(14)
Z	4
d_{calc}/g cm^{-3}	1.374
Absorption coefficient/mm^{-1}	0.721
F(000)	1292
Diffractometer	Enraf-Nonius CAD-4
Temperature/K	293
Radiation (λ/Å)	Graphite monochromator, Mo-Kα (0.71073)
Scanning technique	ω/2θ
Peak width/deg	1.1 + 0.35tan θ
Scan rate (min/max)/deg min^{-1}	1.2/16
θ range/deg	2.19—27.96
Range of indices	$-2 < h < 20$, $0 < k < 30$, $0 < l < 11$

Parameter	Data and conditions of X-ray study
Number of measured reflections	4181
Number of independent reflections	3882 (R_{int} = 0.0324)
Absorption correction	Empirical (ψ scanning technique)
Transmission (min/max)	0.8634/0.7317
Methods of solution	Direct
Method of refinement	Full-matrix least-squares based on F^2
Refinement of hydrogen atoms	All H atoms were placed in calculated positions (d_{C-H} = 0.93 Å for aromatic H atoms and 0.97 Å for the remaining H atoms) and refined using the riding model
Number of reflections used in the least-squares refinement/number of parameters	3868/347
GOF based on F^2	1.005
R ($I > 2\sigma(I)$)	R_1 = 0.0317, wR_2 = 0.0789
R (using all data)	R_1 = 0.0588, wR_2 = 0.0883
Flack's parameter	0.02(4)
Extinction coefficient	0.0000(4)
Electron density (min/max)/e · Å^{-3}	0.498/−0.603

(decomp.) $[\alpha]_D^{20}$ −50.0° (*c* 1.2, MeOH). Found (%): C, 60.57; H, 6.37; N, 8.79. $C_{29.2}H_{36.8}ClN_{3.6}Pd$. Calculated (%): C, 60.46; H, 6.39; N, 8.69.

^{1}H NMR (methanol-d$_4$), δ, (S_CR_N,*SS*)-**3a**: 1.267 (d, 3 H, CHMe$_2$, $^3J_{HH}$ = 6.4 Hz); 1.295 (d, 3 H, CHMe$_2$, $^3J_{HH}$ = 6.5 Hz); 1.727 (d, 3 H, α-Me, $^3J_{HH}$ = 6.7 Hz); 3.068 (m, 1 H, CHMe$_2$, $^3J_{HH}$ = 6.4 and 6.5 Hz); 4.124 (q, 1 H, C(α)H of the palladacycle, $^3J_{HH}$ = 6.7 Hz); 4.251 and 4.302 (AB system, 2 H, C(α)H, Stien, $^3J_{AB}$ = 11.6 Hz); 6.75—7.33 (m, 17 H, H arom.*); free Stien: 3.96 (br.s, 0.6 H, C(α)H).

^{1}H NMR (acetonitrile-d$_3$), δ, (S_CR_N,*SS*)-**3a**: 1.258 (d, 3 H, CHMe$_2$, $^3J_{HH}$ = 6.4 Hz); 1.286 (d, 3 H, CHMe$_2$, $^3J_{HH}$ = 6.5 Hz); 1.742 (d, 3 H, α-Me, $^3J_{HH}$ = 6.6 Hz); 2.822 (br.dd, 1 H, N(3)H$_{ax}$, $^2J_{HNH}$ = 10.9 Hz, $^3J_{HN-CH}$ = 10.0 Hz); 2.940 (m, 1 H, CHMe$_2$, $^3J_{HH}$ = 6.4 and 6.5 Hz, $^3J_{HC-NH}$ = 5.5 Hz); 4.055 (br.dd, 1 H, N(2)H$_{ax}$, $^2J_{HNH}$ = 10.3 Hz, $^3J_{HN-CH}$ = 10.5 Hz); 4.100 (q, 1 H, C(α)H of the palladacycle, $^3J_{HH}$ = 6.6 Hz); 4.315 (m, 2 H, C(α)H, Stien); 4.518 (br.d, 1 H, N(2)H$_{eq}$, $^2J_{HNH}$ = 10.3 Hz); 5.85 (br.d, 1 H, N(3)H$_{eq}$, $^2J_{HNH}$ = 10.9 Hz); 6.270 (br.d, 1 H, N(1)H of the palladacycle, $^3J_{HN-CH}$ = 5.5 Hz); 6.75—7.33 (m, 17 H, H arom.*); free Stien: 3.95 (br.s, 0.6 H, C(α)H); 2.45 (br.d, NH$_2$).

^{1}H NMR (DMSO-d$_6$, 40 °C), δ, (S_CR_N,*SS*)-**3a**: 1.247 (d, 3 H, CHMe$_2$, $^3J_{HH}$ = 6.4 Hz); 1.254 (d, 3 H, CHMe$_2$, $^3J_{HH}$ = 6.4 Hz); 1.693 (d, 3 H, α-Me, $^3J_{HH}$ = 6.6 Hz); 3.058 (m, 1 H, CHMe$_2$, $^3J_{HH}$ = 6.4 Hz, $^3J_{HC-NH}$ = 5.4 Hz); 3.934 (br.dd, 1 H, N(2)H$_{ax}$, $^2J_{HNH}$ = 12.1 Hz, $^3J_{HN-CH}$ = 9.0 Hz); 4.119 (q, 1 H, C(α)H of the palladacycle, $^3J_{HH}$ = 6.6 Hz); 4.222 (m, 2 H, C(α)H, Stien); 5.147 (br.dd, 1 H, N(3)H$_{ax}$, $^2J_{HNH}$ = 9.0 Hz, $^3J_{HN-CH}$ = 12.0 Hz); 5.225 (br.d, 1 H, N(2)H$_{eq}$, $^2J_{HNH}$ = 12.1 Hz); 5.524 (br.d, 1 H, N(3)H$_{eq}$, $^2J_{HNH}$ = 9.0 Hz); 6.051 (d, 1 H, N(1)H of the palladacycle, $^3J_{HN-CH}$ = 5.4 Hz); 7.15—7.40 (m, 13 H, Ph, Stien*); aromatic protons of the palladacycle: 6.774 (dt, 1 H, C(5)H, $^3J_{HH}$ = 7.4 Hz, $^4J_{HH}$ = 1.4 Hz); 6.911 (dt, 1 H, C(4)H, $^3J_{HH}$ = 7.2 Hz, $^4J_{HH}$ = 0.8 Hz); 6.938 (dd, 1 H, C(3)H, $^3J_{HH}$ = 7.6 Hz, $^4J_{HH}$ = 1.6 Hz); 7.040 (d, 1 H, C(6)H, $^3J_{HH}$ = 7.2 Hz); free Stien: 3.870 (br.s, 0.6 H, C(α)H).

C (Pd : Stien = 1 : 3). A solution of six equivalents of racemic stilbenediamine (0.591 g, 2.781 mmol) in MeOH (3 mL) was added to a suspension of dimer (S_CR_N)-**2** (0.282 g, 0.463 mmol) in anhydrous MeOH (4 mL). After stirring under argon for 1 h, the reaction mixture was filtered and concentrated on a rotary evaporator. The resulting oil was dissolved with weak heating in dry MeCN (4 mL) and allowed to slowly crystallize upon cooling. After 2 days, a colorless crystalline precipitate (0.432 g) was filtered off. After its recrystallization from dry MeCN in the presence of MeOH traces, the indi-

* The signals from the aromatic protons of complex **3a** and those of the free diamine molecule overlap.

* The signals from the aromatic protons and those of the coordinated diamine molecule overlap.

Table 4. Coordinates of nonhydrogen atoms ($\times 10^4$) and equivalent isotropic thermal parameters ($U_{eq} \cdot 10^3$) for the (S_CR_N,*SS*)-**3a** · 0.5(*SS*)-Stien complex

Atom	*x*	*y*	*z*	U_{eq}/Å^2
Pd(1)	3784(1)	8092(1)	8233(1)	31(1)
Cl(1)	3146(1)	8054(1)	3516(2)	58(1)
N(1)	4372(2)	7572(2)	6541(5)	35(1)
N(2)	2489(2)	8108(2)	7253(5)	44(1)
N(3)	3208(2)	8600(2)	9937(5)	35(1)
C(1)	4982(3)	8140(2)	9072(5)	34(1)
C(2)	5267(3)	8376(2)	10515(6)	42(1)
C(3)	6140(4)	8411(3)	10894(6)	53(1)
C(4)	6758(4)	8197(3)	9868(7)	55(2)
C(5)	6496(3)	7945(2)	8455(8)	48(2)
C(6)	5614(3)	7926(2)	8030(6)	38(1)
C(7)	5332(3)	7700(2)	6458(6)	39(1)
C(8)	5500(4)	8119(3)	5126(6)	57(2)
C(9)	4199(3)	6945(2)	6718(7)	40(1)
C(10)	4450(4)	6740(2)	8381(7)	54(1)
C(11)	3254(4)	6808(2)	6352(7)	49(1)
C(12)	2035(3)	8615(2)	7910(6)	35(1)
C(13)	2239(3)	8632(2)	9734(6)	33(1)
C(14)	1052(3)	8615(2)	7634(6)	39(1)
C(15)	556(3)	8134(3)	7889(6)	48(1)
C(16)	−348(4)	8153(3)	7683(7)	61(2)
C(17)	−740(4)	8645(4)	7243(8)	69(2)
C(18)	−260(4)	9120(4)	6951(10)	79(2)
C(19)	641(4)	9114(3)	7136(8)	62(2)
C(20)	1860(3)	9142(2)	10570(6)	36(1)
C(21)	1456(3)	9072(3)	12029(7)	48(1)
C(22)	1092(4)	9535(3)	12822(8)	69(2)
C(23)	1133(5)	10060(3)	12195(9)	72(2)
C(24)	1538(4)	10152(3)	10770(10)	70(2)
C(25)	1907(4)	9688(2)	9965(8)	52(2)
N(2′)	4107(4)	9814(3)	10292(8)	77(2)
C(1′)	4015(4)	9923(2)	7406(8)	51(1)
C(2′)	3872(5)	9529(3)	6243(9)	72(2)
C(3′)	3331(7)	9643(5)	4961(13)	118(4)
C(4′)	2944(7)	10190(5)	4899(16)	125(4)
C(5′)	3101(5)	10579(4)	6031(14)	106(4)
C(6′)	3611(4)	10456(3)	7278(10)	68(2)
C(7′)	4611(4)	9798(2)	8818(8)	54(2)

vidual diastereomer of the solvated complex (S_CR_N,*SS*)-**3a** · 0.5(*SS*)-Stien (**4**) was isolated in 66% yield (with respect to Pd and diamine; 0.382 g, 0.614 mmol), m.p. 201–203 °C (decomp.), $[\alpha]_D^{20}$ −39.4° (*c* 1.7, MeOH). Found (%): C, 61.45; H, 6.51; N, 9.03. $C_{32}H_{40}ClN_4Pd$. Calculated (%): C, 61.74; H, 6.48; N, 9.00.

The ^{1}H NMR spectrum of the complex measured in DMSO-d_6 is identical to that of the sample prepared according to method ***B*** except for the intensity of the C(α)H signal of free diamine (1 H).

Isolation of (*SS*)-stilbenediamine. 1 *M* HCl (5 mL) was added to a suspension of the individual diastereomer (S_CR_N,*SS*)-**3a** · 0.5(*SS*)-Stien (0.212 g, 0.341 mmol), which was prepared according to method *C*, in dichloromethane (10 mL). The reaction mixture was vigorously shaken for 5 min. Then the aqueous layer was separated and extracted with CH_2Cl_2 three times (3×5 mL) to separate the resolving agent (see below). The aqueous layer was concentrated to dryness. Slow addition of a concentrated KOH solution to an aqueous solution of diamine dihydrochloride upon cooling afforded free diamine, which was thoroughly extracted with benzene (4×10 mL). After drying over KOH, the combined organic extracts were concentrated and diamine was precipitated by adding hexane upon cooling. (*SS*)-Stilbenediamine was obtained in a yield of 0.0923 g (0.435 mmol, 85%), $[\alpha]_D^{20}$ −106.2° (*c* 0.8, MeOH) (published data:[42] $[\alpha]_D^{20}$ −106.5° (*c* 1.09, MeOH)).

Regeneration of resolving agent (S_CR_N)-2. The combined organic extracts (after displacement of diamine) were dried over Na_2SO_4, concentrated, and then purified by chromatography on a short column (60×20 mm) with silica gel (10 : 1 benzene–acetone mixture as the eluent). After drying *in vacuo*, chromatographically pure dimer (R_CS_N)-**2** was recovered in 95% yield (0.0985 g, 0.162 mmol).

X-ray diffraction study of the (S_CR_N,*SS*)-3a · 0.5(*SS*)-Stien adduct. The principal characteristics of X-ray diffraction study are given in Table 3. The structure was solved and refined using the SHELXL-86 [66] and SHELXL-93 [67] program packages. The structure was solved by direct methods and refined anisotropically by the full-matrix least-squares method based on F^2. The positions of all hydrogen atoms were located from the difference Fourier synthesis and included in the least-squares refinement using the riding model. The following weighting scheme was used in the refinement: $w = 1/\sigma^2(F) + 0.000028(F^2)$. The absolute configuration of the complex was determined in the course of the standard least-squares refinement using the SHELXL-93 program (Flack's parameter $x = 0.02(4)$) taking into account anomalous X-ray scattering on all atoms. The coordinates of the nonhydrogen atoms and their isotropic thermal parameters are given in Table 4.

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