New homochiral *ortho*-palladated matrix bearing a bulky substituent at the carbon stereocenter

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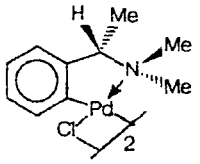
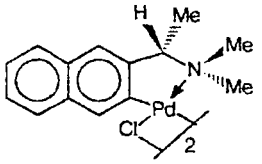
A new homochiral dimeric *ortho*-palladated complex bearing a bulky *tert*-butyl substituent at the carbon stereocenter was synthesized from optically active *N,N*-dimethyl-α-*tert*-butylbenzylamine. Regioselective activation of only the aromatic C—H bond was shown to occur during the cyclometallation process proceeding under very mild conditions due to steric effects. Spectral characteristics of mononuclear derivatives of the new dimeric complex indicate that the five-membered palladacycle exists predominantly in one of two possible chiral conformations with the axial position of the *tert*-butyl substituent.

Key words: *ortho*-palladation, regioselectivity, optical resolution, conformation of palladacycle, chiroptical properties.

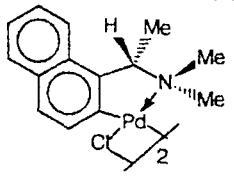
Interest in the use of optically active cyclopalladated complexes (CPC) has been increased recently. These complexes are used for optical resolution of various substrates with ligand properties[1—4] and for determination of their optical purity.[5,6] However, before the beginning of our studies in this area,[7—11] the range of stereoselectors of this class was limited to cyclopalladated derivatives of three *N,N*-dimethyl-α-arylethylamines (**1a—c**) only.



(*S*)-**1a**



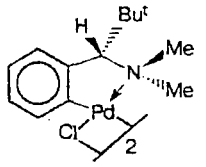
(*S*)-**1b**



(*S*)-**1c**

In an effort to increase the effectiveness of complexes of this type due to their structural modification, we studied the ability of a wide series of previously obtained[12—14] CPC (mainly *N**-chiral) to discriminate enantiomers using a model reaction of the formation of complexes between CPC and racemic monodentate phosphine Bu^t(Ph)PMe.[10]

One of the important results of this work was the observation of certain advantages of the cyclopalladated derivative of *N,N*-dimethyl-α-*tert*-butylbenzylamine (**2**), which was obtained previously[2] in the racemic form and is the sterically more hindered α-Bu^t-substituted analog of the known complex **1a**.



(*S*)*-**2**

First, it is capable of substantially greater chiral recognition and, hence, can be used as a more efficient resolving agent; second, the resolution of signals of diastereomeric monophosphine adducts in $^{31}P\{^1H\}$ NMR spectra is considerably better in the case of α-Bu^t-substituted derivatives, which allows the new *ortho*-palladated matrix **2** to be used as a reagent for the determination of the optical purity of phosphines.

Both directions of the practical use of the new *ortho*-palladated matrix **2** require preparation of the coomplex in an optically pure state, which is the purpose of the present work.

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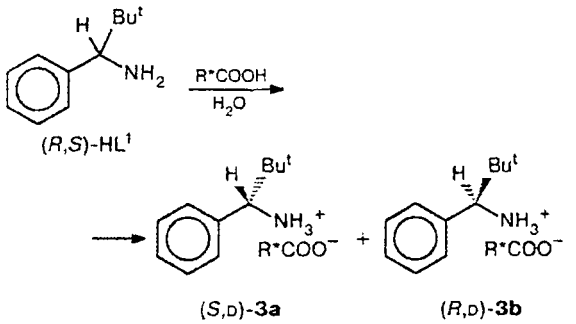
Results and Discussion

Two approaches to homochiral CPC are possible: 1) synthesis of a racemic dimeric cyclopalladated complex followed by its optical resolution using an appropriate auxilliary chiral ligand; this methodology has been widely used;[14–18] 2) preparation of the starting ligand in the optically active form followed by its cyclopalladation.

In this work, we used the second approach, because it allows one not only to avoid losses of expensive palladium at the stages of separation of diastereomeric complexes by crystallization, but also to establish directly the absolute configuration (AC) of the formed CPC from the known configuration of the starting primary amine.

Synthesis of the starting ligand. Several methods of the asymmetric synthesis of α-*tert*-butylbenzylamine are known;[19–21] however, all of them are difficult and multistep[19,20] and most often do not give the required amine in the homochiral state.[20,21] Therefore, for the preparation of an enantiomerically pure ligand, we used the optical resolution of racemic α-*tert*-butylbenzylamine synthesized by the reduction of pivalophenone oxime under previously described[22] conditions. As we know there is only one method for the resolution of α-*tert*-butylbenzylamine based on the fractional crystallization of diastereomeric salts with *N*-acetyl-L-leucine from water. This method makes it possible to isolate only one diastereomer of the salt containing the amine in the (*R*)-configuration in 42% yield and with specific rotation $[\alpha]_D$ −7.2° (*c* 4, MeOH) after two recrystallizations.[23]

Using *N*-acetyl-D-leucine and introducing a seeding of the pure diastereomer of the salt, we obtained (*S*)-α-*tert*-butylbenzylammonium *N*-acetyl-D-leucinate **3a** in 43% yield with specific rotation $[\alpha]_D$ +6.85° (*c* 4, MeOH). This value corresponds to a 98.2% enantiomeric excess of (*S*)-HL[1] according to the data of HPLC on a chiral column (see below).



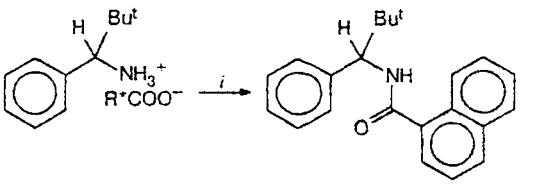
For the purpose of increasing the overall yield of the optically active amine HL[1], we isolated the second diastereomer of its acetylleucinate salt **3b** from mother liquors. This diastereomer contains the amine in the (*R*)-configuration with the specific rotation $[\alpha]_D$ +11.0° (*c* 4, MeOH) corresponding to 98.2% *ee* (*R*)-amine.

However, it should be mentioned that water is not the optimum solvent for separation of diastereomeric salts **3a,b**. Their similar solubility often results in crystallization of the second diastereomer after partial precipitation of the first diastereomer, the necessity of multiple boiling of aqueous solutions results in partial decomposition of the salt, and drying samples before measurements of the specific rotation takes a lot of time. Therefore, we also tried crystallizing diastereomers from ethanol. Double recrystallization of a mixture of salts **3a,b** enriched in the (D,*R*)-diastereomer by only 10–15% from ethanol using individual diastereomer (D,*R*)-**3b** for seeding gave (*R*)-α-*tert*-butylbenzylammonium *N*-acetyl-D-leucinate with an optical purity of 91% *ee* in 42% yield.

The optically active tertiary amine (*S*)-HL[2], which was used as a ligand in the synthesis of the dimeric cyclopalladated complex (*S,S*)-**2**, was obtained by exhaustive *N*-methylation of the thus-resolved primary amine under standard conditions.[24]

The optical resolution of the primary amine HL[1] was monitored by HPLC on chiral columns. The use of this method of monitoring is especially important in this case, because the low values of specific rotation typical of mixtures of diastereomers **3a,b** stop to adequately reflect their composition due to partial decomposition of the samples under the conditions of recrystallization from boiling water. Thus, the comparison of the observed $[\alpha]_D$ values with the enantiomeric composition (determined by HPLC) of α-*tert*-butylbenzylamine in some fractions of its *N*-acetyl-D-leucinate salt **3** showed that the error in the determination of the optical purity of the amine by specific rotation of its salt can reach ±12%.

It is noteworthy that chromatographic methods for the determination of optical purity and the separation of enantiomers on chiral stationary phases have been widely developed recently.[25] Chiral recognition of α-arylalkylamines is especially efficient on stationary phases of the π-acceptor type[26] after the appropriate derivatization of the amine. 1-Naphthoylamide derivatives are especially convenient for analysis of the enantiomeric composition of these substrates due to their high selectivity in the separation of enantiomers and relatively high chromatographic retention.[27] Therefore, 1-naphthoylamide derivative **4** generated *in situ* was chosen for monitoring the enantiomeric composition of α-*tert*-butylbenzylamine in individual fractions of its salt **3** with *N*-acetyl-D-leucine.



i. 1) 1 *M* $NaOH_{aq}$/toluene, 2) 1-NaphthCOCl

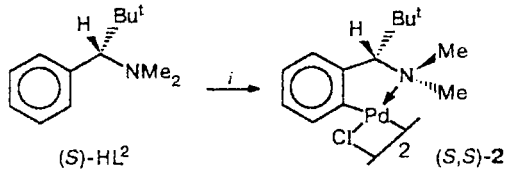
3-Aminopropylsilylated silica gel, which was chirally modified by covalent binding with a chiral selector* using the methodology described in Refs. 27 and 28, was used as the sorbent for HPLC. Its selectivity, as a whole, is close to that of commercially available chiral stationary phases of the π-acceptor type known as the Pirkle phases.

The possibility of estimating the absolute configuration (AC) of the resolved amine is an important advantage of the use of HPLC on chiral columns. The wide experience in this field and considerations of the established mechanism of recognition of enantiomers in chromatography[27,28] make it possible to confidently correlate the retention times of the two enantiomers with their absolute configurations.

The observed peaks were assigned to the (*R*)- and (*S*)-enantiomers of α-*tert*-butylbenzylamine on the basis of a preliminary study of a mixture of enantiomers of α-methylbenzylamine with known enantiomeric composition (*R*)/(*S*) = 1 : 3 on the same chiral support. The fact that the experimentally observed retention times of two enantiomers of α-*tert*-butylbenzylamine 1-naphthoylamide, **4a** and **4b**, are equal to 13.3 and 17.5 min allow one to assign the absolute configurations (*R*) and (*S*) to compounds **4a** and **4b**, respectively. Thus, we obtained an independent confirmation of the (*S*)-configuration of α-*tert*-butylbenzylamine that forms the diastereomeric salt with *N*-acetyl-D-leucine (**3a**), which is less soluble in water and characterized by $[\alpha]_D$ values of 6.4—6.8°. The absolute (*R*)-configuration should be assigned to the amine forming diastereomer **3b**, which is more soluble in water and whose specific rotation is as high as +11°.

It is of interest to note that the selectivity of separation of enantiomers of 1-naphthoylamides **4a,b** is considerably greater than that of the α-methylbenzyl analogs: when the Me group in the α-benzyl position is replaced by a Bu^t group, the selectivity increases from α = 1.21 for the derivative of α-methylbenzylamine to α = 1.37 for α-*tert*-butylbenzylamine. This is evidence for more efficient chiral recognition of substrates with a *tert*-butyl group at the stereogenic center.

Cyclopalladation of (*S*)-*N*,*N*-dimethyl-α-*tert*-butylbenzylamine. The reaction of direct intramolecular palladation of amine (*S*)-HL^2 was carried out under the mild conditions that were used previously for the racemic amine,[2] by the action of Li_2PdCl_4 in methanol at 0—2 °C in the presence of excess sodium acetate as the base.

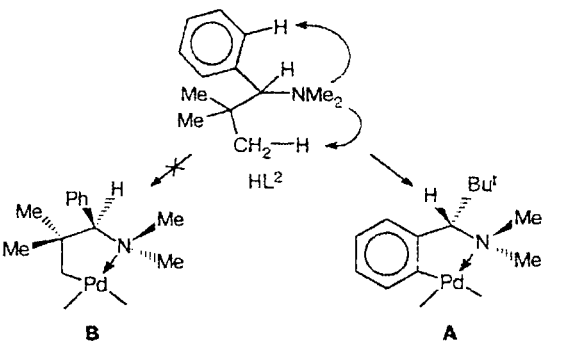


(*S*)-HL^2 (*S*,*S*)-**2**

i. Li_2PdCl_4, AcONa, MeOH, 0—2 °C

The easy activation of the aromatic C—H bond is likely caused by the presence of the bulky α-Bu^t substituent in this substrate. The similar effect of "steric compression," which was observed for the first time for cyclopalladation of phosphine ligands,[29] is especially pronounced in the case of secondary benzylamines.[14,30]

In practical aspect, it is also important that cyclopalladation of the tertiary amine HL^2 occurs completely regioselectively despite the fundamental possibility that two different palladacycles of the same size could form.



Even when the conditions most appropriate for the activation of the aliphatic C—H bond of the Bu^t group in the secondary amine[2] are used, in the case of the analogous tertiary amine HL^2, we observed no indication of the formation of the regioisomeric complex with a **B** type palladacycle.

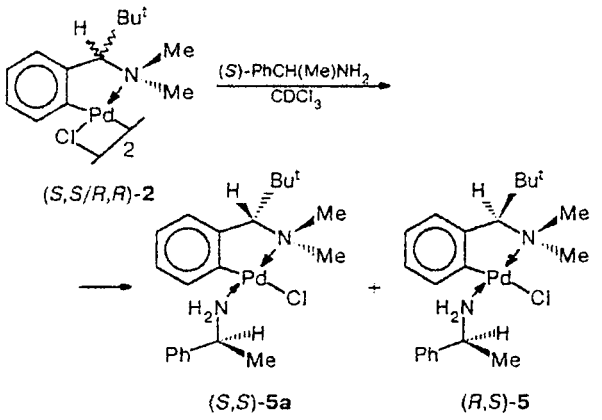
The (*S*,*S*)-**2** complex in the crystalline state was obtained in 78% yield, and its structure was confirmed by both elemental analysis and ^{1}H NMR spectroscopy. The spectral data indicate that it exists in solutions as a mixture of *cis*/*trans*-isomers in ~1 : 2 ratio.

The dimeric structure of the primary product of the *ortho*-palladation of the amine (*S*)-HL^2 makes it fundamentally possible to increase its optical purity by separating minor amounts of the enantiomeric form as the *meso*-isomer (*R*,*S*)-**2** from the main diastereomer (*S*,*S*)-**2**, for example, during crystallization. In fact, when the amine (*S*)-HL^2 with an optical purity of 91—93% *ee* (*S*) was used in cyclopalladation, we succeeded in obtaining the dimeric (*S*,*S*)-**2** complex in the homochiral state after only one recrystallization.

In order to confirm the complete optical purity of this complex by ^{1}H NMR, the spectrum of racemic dimer (*SS*/*RR*)-**2** was first measured in the presence of excess (*S*)-α-methylbenzylamine (HL^3) as the auxilliary homochiral ligand. Under these conditions, a mixture of two diastereomers of the mononuclear adduct with the amine HL^3, (*S*,*S*)-**5a** and (*R*,*S*)-**5b**, are formed in solution.

Good resolution of signals of the majority of the aliphatic protons (as well as the aromatic H(6) proton that is adjacent to the palladation site) belonging to

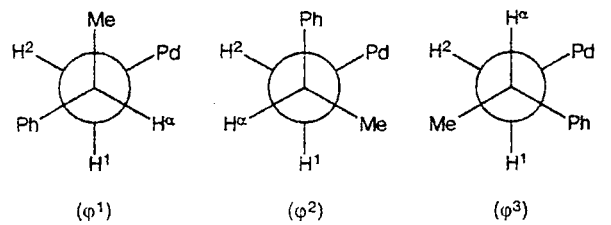
* For a detailed description of preparation of this and other similar enantioselective sorbents, see O. R. Malyshev and V. G. Vinogradov, *J. Chromatogr.*, 1997, in press.



diastereomeric complexes (*S,S*)-**5a** and (*R,S*)-**5b**, their insignificant overlapping with signals of free (*S*)-α-methylbenzylamine (Table 1), and the absence of any difficulties caused by exchange between the *N*-coordinated and free monodentate amine HL^3 create a reliable basis for the determination of the optical purity of dimeric complex (*S,S*)-**2** by ^1H NMR.

The ^1H NMR spectrum of complex (*S,S*)-**2** obtained from the optically active amine (HL^2) was recorded under the same conditions and contained only one set of signals corresponding to diastereomer (*S,S*)-**5a**. No indications of the existence of the second diastereomer (*R,S*)-**5b** in the solution were observed even under conditions that allowed satellites from ^{13}C nuclei to be detected with a good signal to noise ratio. This is evidence for the homochiral state of complex (*S,S*)-**2** achieved after one recrystallization due to the difference in solubility between its (*S,S*)- and (*R,S*)-diastereomers.

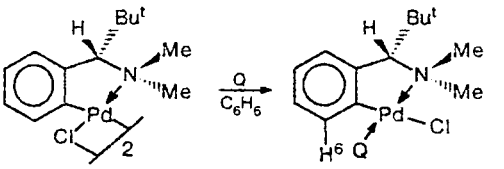
For more reliable identification of the signals from the two diastereomers of mononuclear complex **5a,b** generated *in situ* according to our methodology of the optical purity determination of dimeric CPC (*S,S*)-**2**, one of the two diastereomers, (*S,S*)-**5a**, was isolated in the crystalline state and characterized by standard methods (Table 1, Experimental). The most remarkable feature of the ^1H NMR spectrum of complex (*S,S*)-**5a** is the fact that the two spin-spin coupling constants of the interaction of the α-methine proton of the coordinated α-methylbenzylamine with two diastereotopic protons of the NH_2 group differ sharply: this proton signal appears as a double doublet of quartets at δ 4.289 with the values $^3J_{CH-NH}$ = 11.7 and 2.4 Hz. This indicates that the rotational mobility of this monodentate ligand is considerably restricted in the NMR time scale. It is evident from the Newman projections (φ^1—φ^3)



relative to the α-C—N bond presented below for the three most real rotamers of this ligand that the $^3J_{CH-NH}$ constants can be strikingly different only in rotamers φ^1 and φ^3, while the symmetric orientation of the α-methine proton in the φ^2 form should result in equal values of $^3J_{CH-NH}$.

The choice between rotamers φ^1 and φ^3 can be based on the following considerations. When α-methylbenzylamine coordinates with palladium(II), the signal of the protons of the α-Me group undergoes a noticeable downfield shift: in the ^1H NMR spectrum of complex (*S,S*)-**5a** generated *in situ*, it is observed at δ 1.76 for the coordinated amine and at δ 1.38 for the free amine. This shift (Δδ 0.38) is usually characteristic of protons oriented above the metal center. By contrast, no similar effect is observed for the *ortho*-protons of the phenyl ring: the signals of the Ph ring of both coordinated and free α-methylbenzylamine are observed as an unresolved multiplet in the narrow range of δ 7.20—7.45. This suggests that α-methylbenzylamine coordinated with palladium exists in complex (*S,S*)-**5a** predominantly as the least sterically hindered conformer φ^1.

Other mononuclear derivatives of dimer (*S,S*)-2. In order to confirm the site of metallation in dimer (*S,S*)-**2** and to estimate the effect of the bulky Bu^t substituent on the conformation of the palladacycle formed, we also obtained two other mononuclear derivatives of this complex: one with pyridine (**6**) and one with triphenylphosphine (**7**). They were synthesized by the standard reactions of cleavage of the chloride bridges in the initial dimer:



The ^1H NMR spectra of adducts **6** and **7** unambiguously confirm the *ortho*-palladated structure of these mononuclear complexes (and, hence, of the starting dimer **2**). The resonance region of the aromatic protons has four well resolved signals with the multiplicity expected for an *ortho*-disubstituted phenyl ring, while the singlet with integral intensity 9 H corresponds to the intact α-*tert*-butyl group. In the ^1H NMR spectra of mononuclear complexes **6** and **7**, a significant upfield shift of the signals of the protons closest to the site of palladation of the aromatic ring is observed: the signals of the C(6)—H proton in the spectrum of pyridine adduct **6** and the C(6)—H and C(5)—H protons in the spectrum of triphenylphosphine adduct **7** are observed at δ 5.99, 6.30, and 6.40, respectively, while in the spectrum of the free amine HL^2, they are observed at

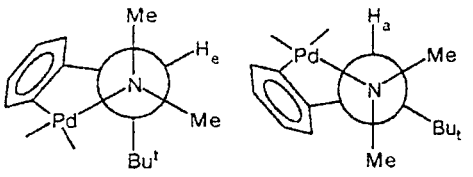
Table 1. ^{1}H NMR spectra of cyclopalladated complexes based on *N,N*-dimethyl-α-*tert*-butylbenzylamine ($CDCl_3$, δ, *J*/Hz)

Complex	C*-substituents		N*-substituents		Aromatic protons				Signals of additional ligand
	α-Bu^t (9 H)	α-CH (1 H)	NMe_a (3 H)	NMe_e (3 H)	H(6) (1 H)	H(5) (1 H)	H(4) (1 H)	H(3) (1 H)	
					$^3J_{HH}$, $^4J_{HH}$				
(*S,S*)-**2**[a]	1.411 s	3.180 s	2.838 s, 2.857 s		7.123 (dd, $^3J_{HH}$= 7.7)	6.82—6.93 (m, 3 H)			—
	1.406 s	3.180 s	2.779 s, 2.852 s		7.174 (dd, $^3J_{HH}$= 7.7)	6.82—6.93 (m, 3 H)			—
(*S,S*)-**5a**[b]	1.353 s	3.203 s	2.763 s	2.959 s	6.718 m	6.90—7.05 (m, 6 H)[c]			HL^3: 1.835 (d, 3 H, α-Me, $^3J_{HH}$=6.9); 2.88 (br.m, 1 H, NH(1)); 3.699 (br.t, 1 H, NH(2), J_{av}=11.2); 4.281 (m, 1 H, α-CH); 7.20—7.45 (m, Ph)[d,e]
(*R,S*)-**5b**[b]	1.296 s	3.161 s	2.742 s	2.920 s	6.592 (dd, $^3J_{HH}$= 7.4, $^4J_{HH}$= 1.4)	6.85—7.05 (m, 6 H)[c]			HL^3: 1.708 (d, 3 H, α-Me, $^3J_{HH}$=6.9); 2.9 (br.m, 1 H, NH(2)) 3.563 (br.d, 1 H, NH(1), J_{av}=10.5); 4.570 (ddq, 1 H, $^3J_{HH}$=6.9, α-CH, $^3J_{CH-NH(2)}$=9.9, $^3J_{CH-NH(1)}$=4.5); 7.20—7.45 (m, Ph)[d,e]
(*S,S*)-**5a**[f]	1.354 s	3.202 s	2.763 s	2.958 s	6.718 m	6.93—7.03 (m, 3 H)			HL^3: 1.756 (d, 3 H, α-Me, $^3J_{HH}$=6.8); 2.869 (br.d, 1 H, NH(1), J_{av}=10.6); 3.703 (br.t, 1 H, NH(2), $^3J_{NH-CH}$=11.7, $^2J_{NH-NH}$=10.6); 4.278 (ddq, 1 H, α-CH, $^3J_{HH}$=6.8, $^3J_{CH-NH(2)}$=11.7, $^3J_{CH-NH(1)}$=2.4); 7.2—7.4 (m, 5 H, Ph)[g]
(*S,S*)-**5a**	1.363 s	3.216 s	2.775 s	2.969 s	6.719 m	6.93—7.03 (m, 3 H)			HL^3: 1.847 (d, 3 H, α-Me, $^3J_{HH}$=6.7); 2.794 (br.d, 1 H, NH(1)); 3.709 (br.t, 1 H, NH(2), $^3J_{NH-CH}$=11.7, $^2J_{NH-NH}$=10.8); 4.289 (ddq, 1 H, α-CH, $^3J_{HH}$=6.7, $^3J_{CH-NH}$=11.7, $^3J_{CH-NH}$=2.4); 7.32—7.42 (m, 5 H, Ph)
(*S*)-**6**	1.401 s	3.244 s	2.824 s	2.981 s	5.991 (dd, $^3J_{HH}$= 7.7, $^4J_{HH}$= 1.2)	6.734 (dt, ^3J= 7.7 and 7.3, ^4J= 1.5)	6.938 (dt, ^3J= 7.3 and 7.5, ^4J= 1.2)	6.975 (dd, ^3J=7.5, ^4J=1.5)	Py: 7.373 (m, 2 H, β-H); 7.813 (t.t, 1 H, γ-H, $^3J_{HH}$=7.7, $^4J_{HH}$=1.7); 8.884 (m, 2 H, α-H)
(*S*)-**7**	1.446 s	3.305 (d, $^4J_{PH}$= 5.4)	2.653 s	3.029 (d, $^4J_{PH}$= 3.3)	6.302 (dt, J_{PH}= 6.5, $^3J_{HH}$= 7.6, $^4J_{HH}$= 1.1)	6.402 (t, ^3J= 7.5)	6.791 (t, ^3J= 7.5)	6.985 (dd, ^3J=7.4, ^4J=1.5)	PPh_3: 7.32—7.44 (m, 9 H, *m*-H, *p*-H); 7.724 (m, 6 H, *o*-H, J_{PH}=11.3)

[a] The spectrum of the dimer contains two sets of signals in a ratio of ~2 : 1 corresponding to the *trans*- and *cis*-isomers. [b] The spectral parameters of two diastereomeric complexes generated *in situ* by the treatment of racemic dimer (*RR/SS*)-**2** with optically pure (*S*)-α-methylbenzylamine HL^3 (10 molar equiv.). [c] The signals of three other aromatic protons of the palladated phenyl ring (H(3)—H(5)) are overlapped with each other and with the corresponding signals of another diastereomer of complex **5**. [d] The signals of protons of Ph groups of free and coordinated (*S*)-α-methylbenzylamine in two diastereomers of adduct **5a,b** are overlapped. [e] The signals of excess noncoordinated (*S*)-α-methylbenzylamine (δ): 1.381 (d, 3 H, α-Me, $^3J_{HH}$ = 6.7 Hz); 1.48 (br.s, 2 H, NH_2); 4.105 (q, 1 H, α-CH, $^3J_{HH}$ = 6.7 Hz); 7.32 (m, Ph). [f] The characteristics of one diastereomeric complex generated *in situ* by the treatment of optically active dimer (*S,S*)-**2** with optically pure (*S*)-α-methylbenzylamine (8 molar equiv.) are presented; no signals from the second diastereomer (**5b**) were observed in the spectrum. [g] The signals of protons of Ph groups of free and coordinated (*S*)-α-methylbenzylamine are overlapped; the signals of excess noncoordinated (*S*)-α-methylbenzylamine (δ): 1.382 (d, 3 H, α-Me, $^3J_{HH}$ = 6.6 Hz); 1.537 (br.s, 2 H, NH_2); 4.103 (q, 1 H, α-CH, $^3J_{HH}$ = 6.6 Hz); 7.32 (m, Ph).

δ 7.15—7.25. These effects, caused by the anisotropy of the Py ring (**6**) or PPh groups (**7**), and the detection of the spin-spin coupling constant of the interaction of the C(6)—H proton with the ^{31}P nucleus for triphenylphosphine adduct **7** (J_{PH} = 6.5 Hz) confirm that the additional ligand is *trans*-arranged relative to the *N*-donor atom of the palladacycle.

Important data on specific conformational features of α-arylalkylaminate palladacycles can be obtained from the analysis of the efficiency of the spin-spin interaction of the α-methine proton with the phosphorus nucleus in spectra of adducts with phosphine ligands. The constant $^4J_{PH}$ = 5.4 Hz observed in the ^1H NMR spectrum of the α-Bu^t-substituted complex **7** indicates the predominantly equatorial orientation of the α-methine proton; when it is axially arranged, no spin-spin interaction with the phosphorus nucleus is usually observed.[2,31]



Therefore, the *tert*-butyl substituent occupies the axial position, which corresponds to the predominant λ-conformation of the palladacycle with the (*S*)-configuration of the α-C*-stereocenter. It should be noted that the alternative δ-conformation of the palladacycle should be extremely unfavorable due to the appearance of strong steric repulsion between the equatorial α-*tert*-butyl group and the two *N*-methyl substituents. The λ(*S*)-conformation of the palladacycle can be additionally stabilized due to agostic interaction between palladium and the *tert*-butyl group when the latter is axially oriented. We detected this interaction by X-ray diffraction analysis of dimer (*S,S*)-**2**.*

Since a substantial preference for one of the two possible chiral conformations of the palladacycle is usually considered to be the main condition for CPC to be effective in recognizing enantiomers,[31] it can be proposed that this is the factor that causes the enantioselectivity found previously in the formation of a complex between phosphine Bu^t(Ph)PMe and racemic dimer **2** to be higher than that for the α-methyl-substituted analog.[10] At the present time, we are evaluating the potential of the new homochiral cyclopalladated matrix (*S,S*)-**2** as a reagent for optical resolution of other phosphines and for determining their optical purity.

The chiroptical properties of complexes (*S,S*)-2, (*S*)-5—(*S*)-7 were studied in order to confirm their absolute configuration. For this purpose, we compared the circular dichroism (CD) spectra of dimer (*S,S*)-**2** and their mononuclear derivatives (*S,S*)-**5a**, (*S*)-**6**, and (*S*)-**7** with those of compounds analogous to the previously described derivatives of (*S*)-*N,N*-dimethyl-α-methylbenzylamine with the same configuration.[12,32]

The CD spectra of dimer (*S,S*)-**2** and its mononuclear derivatives were measured in chloroform in the 240—500 nm region (Figs. 1—4, Table 2). It is note-

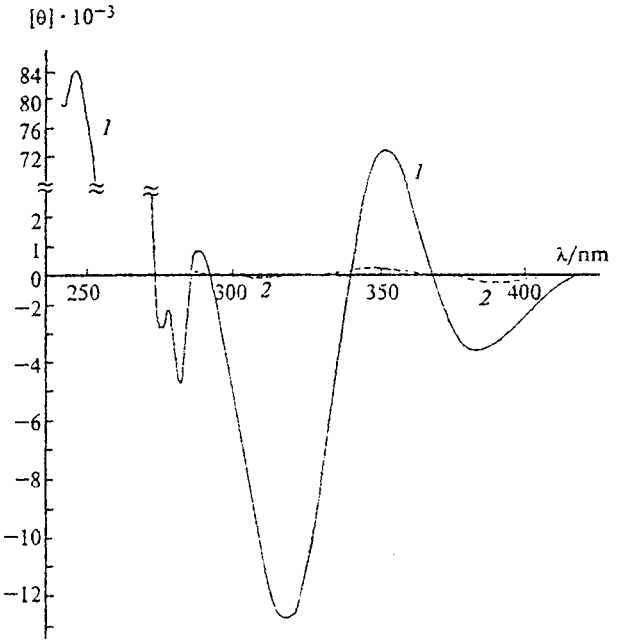


Fig. 1. CD spectra of dimers (*S,S*)-**2** (*1*) and (*S,S*)-**1a** (*2*) in chloroform. The short-wave region of the spectrum of (*S,S*)-**2** is presented in fourfold reduction.

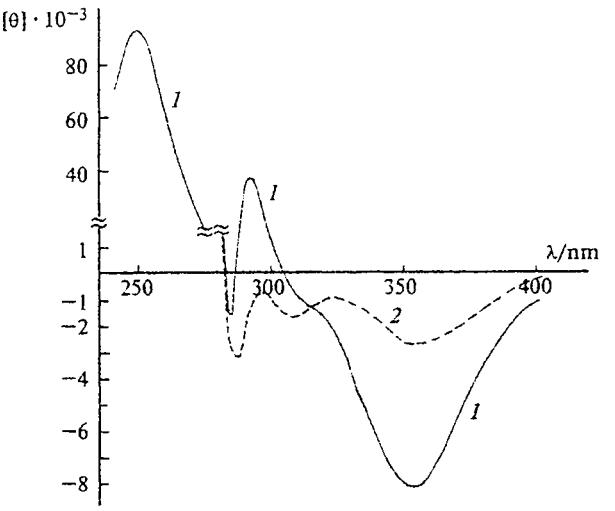


Fig. 2. CD spectra of mononuclear complex (*S*)-**7** (*1*) and the similar adduct of (*S,S*)-**1a** with PPh_3 (*2*) in chloroform. The short-wave region of the spectrum of (*S*)-**7** is presented in tenfold reduction.

* The results of X-ray diffraction analysis of this complex will be published later.

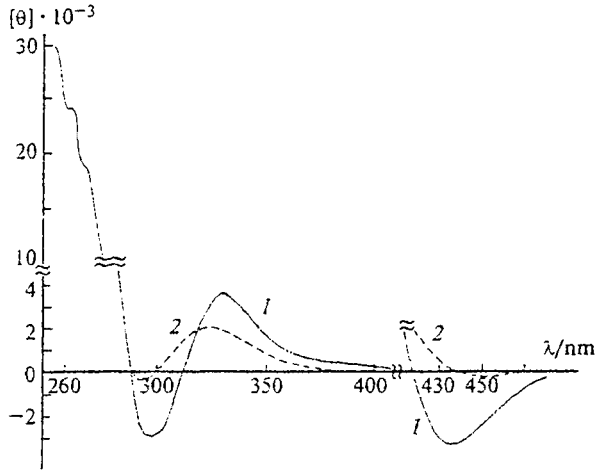


Fig. 3. CD spectra of mononuclear complex (*S*)-**6** (*1*) and similar adducts of (*S,S*)-**1a** with Py (*2*) in chloroform. The short-wave region of the spectrum of (*S*)-**6** is presented in twofold reduction, and the long-wave fragments of the CD spectra of both complexes are amplified 100 times.

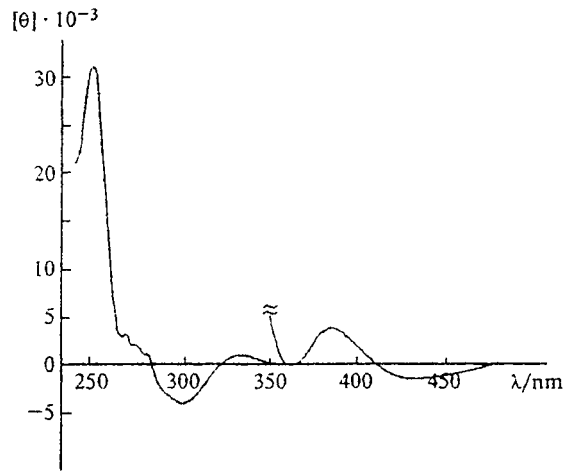
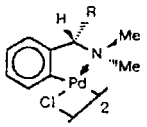
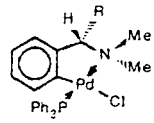
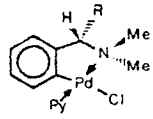
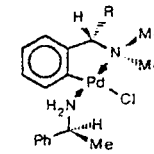


Fig. 4. CD spectrum of mononuclear complex (*S,S*)-**5a** in chloroform. The long-wave fragment of the spectrum is amplified 50 times.

worthy that their correct interpretation is very difficult due to both the complicated character of the chromophore systems and the absence of reliable published information on the electronic structure of complexes of this class. Therefore, all assignments made below are tentative.

The region of the *d-d* electronic transitions of palladium, which are highly sensitive to changes in the electronic and steric surroundings of the metal, is the most convenient one for chiroptical correlations. The coordination complex *trans*-$[PdCl_2(HL^3)_2]$, where HL^3 = (*S*)-α-methylbenzylamine,[33] is the closest model for which electronic transitions have been reasonably correctly assigned on the basis of comparative analysis of the electronic absorption spectra, CD spectra, and magnetic circular dichroism spectra using deconvolution of the spectra into Gaussian components. In the spectra of this model complex with the *trans*-$\{PdN_2Cl_2\}$ chromophore, four bands in the 330—400 nm region were assigned to spin-allowed *d-d* transitions. It can be assumed that they should also manifest themselves approximately in this interval in the CD spectra of the studied complexes with the *trans*-$\{PdN_2CCl\}$ (**5**, **6**), *trans*-(*N,P*)-$\{PdNPCCl\}$ (**7**), and *cis*-$\{PdCNCl_2\}$ (**2**) chromophores.

Table 2. Comparison of chiroptical properties of *ortho*-palladated derivatives of (*S*)-*N,N*-dimethyl-α-*tert*-butylbenzylamine and its α-methyl-substituted analog

Type of complex	R				*k**
	Bu^t		Me		
	λ_{max} /nm	$[\theta]_{max}$	λ_{max} /nm	$[\theta]_{max}$	
			435	36.8	
	383	−2666	389	−216.4	12
	352	4166	346	202.6	21
	318	−11772	306	−64.5	184
	287	820			
	282	−3702			
	246	83896			
	353	−8255	355	−2910	3
	~315 sh.	~−1400	309	−1690	0.8
	292	3625			
	284.5	−1742	287	−3260	0.5
	249.5	91808			
	437	−33.5	453	−2.6	13
	329	3479	325	2027	2
	299	−2989	294	413	7
	263	24726			
	429	−60	—	—	
	384	145			
	361	8			
	330	995			
	299	−4072			

* For convenience of comparison, the last column contains the ratio of molecular ellipticities in the extrema of the bands in the CD spectra of dimers (*S*)-**2** and (*S*)-**1a** and their mononuclear derivatives corresponding to the same electronic transition: $k = [\theta]_{max}^{Bu^t}/[\theta]_{max}^{Me}$.

It can be seen from a comparison of the data presented in Table 2 and Figs. 1—4 that the molecular ellipticity of the bands in the CD spectra of the cyclopalladated derivatives of α-methyl- and α-Bu^t-substituted benzylamines at all comparable wavelengths corresponding to the same electronic transition has the same sign, which suggests that they have the same (S_C) absolute configuration. Therefore, the introduction of a bulky substituent into a palladacycle does not result in qualitative changes in the chiroptical characteristics of the complexes, and the assignment of AC of the

cyclopalladated derivatives of the secondary amine, which was made previously[14] on the basis of the CD spectra, can also considered to be fairly accurate.

The quantitative changes in the parameters of the CD spectra that accompany the replacement of the α-Me group by α-Bu^t agree with the fact that the palladacycle exists predominantly in the λ-conformation. The values of molecular ellipticity at the maximum of the long-wave spin-allowed *d-d* transition (325—355 nm) in the CD spectra of mononuclear adducts **6** (Fig. 3) and **7** (Fig. 2) are 2—3 times higher than the value determined for the α-methyl-substituted analogs. The intensity of the dichroic band at 437 nm in the CD spectrum of complex **6** (this band corresponds to one of the spin-forbidden *d-d* transitions) is 13 times greater than the $[\theta]_{max}$ value for the α-Me-substituted analog. The contrast is more striking for the pair of dimeric complexes (Fig. 1): the molecular ellipticity at the maximum of the dichroic band at 346—352 nm for one of the spin-allowed *d-d* transitions of palladium increases by more than 20 times when the α-methyl group in (*S*)-**1a** is replaced by the α-*tert*-butyl group in the case of (*S*)-**2**. It should be mentioned that the decrease in the molecular ellipticity of the bands in the 280—315 nm region (corresponding to charge-transfer transitions) in the CD spectrum of complex **7** (Fig. 2) is most likely the result of overlap with adjacent, closely arranged dichroic maxima with a higher intensity.

The fact that in the majority of cases in the spectra of *ortho*-palladated derivatives of *N,N*-dimethyl-α-*tert*-butylbenzylamine, the intensity of the dichroic maxima corresponding to the *d-d*-transitions is greater than that of the α-Me-substituted analogs, suggests a large contribution to the optical activity from the bulky α-Bu^t group. This is possible only when it is axially oriented in the λ-conformer; the α-substituent in the equatorial position in the δ-conformer is located rather close to the zero plane, and its contribution to the optical density should be insignificant.

Thus, the chiroptical properties of the *ortho*-palladated derivatives of (*S*)-*N,N*-dimethyl-α-*tert*-butylbenzylamine agree with the data of ^{1}H NMR and also indicate that the palladacycle exists predominantly in the λ(*S*)-conformation with the axially oriented Bu^t substituent at the carbon stereocenter.

Experimental

General conditions. The complex compounds were synthesized and the starting amines were distilled in an atmosphere of argon. Reactions were monitored by TLC on Silufol UV-254 plates.

Solvents. Chloroform was purified by passing it through a short column filled with Al_2O_3 (II degree of activity) prior to use. Benzene was dried over $CaCl_2$, refluxed, and distilled over metallic Na. Anhydrous methanol was obtained by boiling with magnesium methylate followed by distillation. Acetone (special purity grade) and 96% ethanol were used without additional purification.

Reagents. Hydroxylamine hydrochloride (pure grade), a 30% aqueous solution of formaldehyde (pure grade), and D-leucine characterized by specific rotation $[\alpha]_D = -15.1°$ (*c* 2, 6 *N* HCl) were used without additional purification. Formic acid (analytically pure grade) was twice distilled over P_2O_5 in an argon flow. Pyridine dried with KOH was distilled over KOH in an argon flow. (*S*)-α-Methylbenzylamine with specific rotation $[\alpha]_D = -40.8°$ (without solvent) was distilled *in vacuo* above KOH in an argon flow. Triphenylphosphine was twice recrystallized from a benzene—heptane mixture.

Physicochemical studies. ^{1}H NMR spectra were recorded on a Varian VXR-400 spectrometer with a working frequency of 400 MHz in $CDCl_3$ using $SiMe_4$ as the internal standard. Signals were assigned and values of spin-spin coupling constants were estimated using double homonuclear resonance. Circular dichroism spectra of complexes (*S,S*)-**2**, (*S,S*)-**5**, (*S*)-**6**, and (*S*)-**7** were recorded on a JASCO J-720 spectropolarimeter in the range of wavelengths from 240 to 500 nm in chloroform using 0.2- and 1.0-cm cells (CSIF SD*). An AI-EPO polarimeter (VNIEKIProdmash) was used for measuring specific rotation at +22°C.

HPLC experiments were carried out on a "Laboratorni pristroje praha" liquid chromatograph with an HPP-5001 high-pressure pump, a UV VIS LCD-2563 detector, an CI-100 integrator, and a TZ-4620 recorder; an LCI-30 injection valve (with a 3 mL loop), and a Hamilton syringe for injecting a sample (10 mL). A 150×3.3 mm column filled with a sorbent for separation of enantiomers of compounds with π-electron-donating properties was used. The sorbent was prepared by covalent binding of the chiral selector with amino groups of 3-aminopropylsilylylated silica gel Separon-NH_2 with a particle size of 5 mm.

Synthesis of starting compounds

***N*-Acetyl-D-leucine** was obtained by acylation of D-leucine by acetic anhydride under previously described conditions[34] in 45% yield; $[\alpha]_D$ 23.9° (*c* 4, MeOH).

***tert*-Butyl phenyl ketone oxime** was synthesized[35] by the reaction of pivalophenone with hydroxylamine hydrochloride in 78% yield, m.p. 163—164 °C. ^{1}H NMR (60 MHz, $CDCl_3$), δ: 1.15 (s, 9 H, Bu^t); 7.10—7.45 (m, 5 H, Ph); 9.25 (br.s, 1 H, OH).

Racemic **α-*tert*-butylbenzylamine** (HL^1) was obtained by the reduction of *tert*-butyl phenyl ketone oxime with sodium metal in anhydrous methanol according to the known procedure[22] in 84% yield, b.p. 91—92 °C (9 Torr). ^{1}H NMR ($CDCl_3$), δ: 0.946 (s, 9 H, Bu^t); 1.445 (br.s, 2 H, NH_2); 3.703 (s, 1 H, α-CH); 7.2—7.3 (m, 5 H, Ph).

Optical resolution of α-*tert*-butylbenzylamine (HL^1) was carried out similarly to the known procedure[23] with some modifications.

1. An equimolar mixture of diastereomers of **α-*tert*-butylbenzylammonium *N*-acetyl-D-leucinate** (D,*S*/D,*R*)-**3a,b** was obtained by the treatment of a hot solution of *N*-acetyl-D-leucine (2.42 g, 14 mmol) in water (45 mL) with a small excess of racemic α-*tert*-butylbenzylamine (2.54 g, 16 mmol). The crystals that precipitated during slow cooling were filtered off and recrystallized from hot water. (*S*)-α-*tert*-Butylbenzylammonium *N*-acetyl-D-leucinate ((D,*S*)-**3a**, $[\alpha]_D$ +6.9° (*c* 4, MeOH), m.p. 188—190 °C (with decomp.), containing the amine with an optical purity of 98.2±0.1% *ee* (*S*) (according to the HPLC data) was obtained as colorless compact

* Center for Sophisticated Instrument Facilities, Spectropolarymetry Division.

crystals (1.073 g, 43%). (*R*)-α-*tert*-Butylbenzylammonium *N*-acetyl-D-leucinate ((D,*R*)-**3b**, $[\alpha]_D$ +11.0° (*c* 4, MeOH), m.p. (with decomp.) 178—184 °C, containing the amine with an optical purity of +98.2±0.1% *ee* (*R*)) was isolated as thin needle-like crystals (2.12 g, 64%) from the mother liquors of this and similar experiments containing a salt (5.84 g, 17 mmol) with $[\alpha]_D$ 9.8° (*c* 4, MeOH) enriched in the (*R*)-enantiomer of the amine (57% *ee*) after two recrystallizations from water.

2. A mixture of diastereomers of **α-*tert*-butylbenzylammonium *N*-acetyl-D-leucinate** (9.165 g, 53 mmol) enriched in the (*R*)-enantiomer by only 10% was dissolved in boiling ethanol, a seed crystal of the individual diastereomer (D,*R*)-**3b** was introduced, and the mixture was slowly cooled. The obtained mass of colorless needle-like crystals was repeatedly recrystallized from ethanol to give a salt (2.41 g, 42%) containing α-*tert*-butylbenzylamine with an optical purity of 91.0% *ee* (*R*).

3. Several fractions of the salt (D,*S*)-**3a** containing the amine with an optical purity of 91—93% *ee* (*S*) (taken from several resolution experiments) were treated with a cooled aqueous solution of KOH under a benzene layer with cooling. Subsequent thorough extraction with benzene, drying with KOH, and distillation *in vacuo* in an argon flow gave (*S*)-α-*tert*-butylbenzylamine (2.64 g, 88%), b.p. 100—101 °C (13 Torr), R_f 0.53 (Silufol, MeOH/NH_4OH_{aq}, 50 : 1), $[\alpha]_D$ −5.2° (without solvent), optical purity 92% *ee* (*S*). For the published data for the (*R*)-amine with $[\alpha]_D$ +5.6° (without solvent), see Ref. 23.

Determination of optical purity of (*S*)-α-*tert*-butylbenzylammonium *N*-acetyl-D-leucinate by HPLC

Conditions of chromatography. A 2-propanol—heptane (2 : 3 v/v) mixture was used as the mobile phase; the rate of the mobile phase was 0.5 mL min^{-1}; the void volume of the column (V_0 = 1.10 mL) was determined from the elution time of toluene as unretained substance. UV detection was performed at the wavelength λ = 254 nm. The retention times of the two enantiomers of the α-naphthoyl derivative of the primary amine HL[1] (**4a,b**) are equal to 13.33 min for the (*R*)-enantiomer and 17.50 min for the (*S*)-enantiomer; selectivity α = 1.37. A procedure for determining optical purity was developed for the racemic amine.

Procedure of derivatization of amine. A sample of (*R,S*)-α-*tert*-butylbenzylammonium *N*-acetyl-D-leucinate (3—5 mg) was shaken with 1 *M* NaOH (1 mL) and toluene (1 mL), then 1-naphthoyl chloride (5 mL) was added, and the mixture was shaken from time to time for 1 h. Then a sample (0.5 mL) was taken from the organic phase, diluted to 3.5 mL with the mobile phase directly in a syringe, and injected into the chromatographic system.

(*S*)-*N,N*-Dimethyl-α-*tert*-butylbenzylamine was obtained by a procedure similar to that described for the racemic amine[24] by treatment of the primary amine (2.643 g) with 99% formic acid (5 equiv.) and 30% formalin (3 equiv.) with cooling followed by prolonged boiling (12 h). The tertiary amine was obtained in a yield of 2.511 g, 81%, b.p. 105—106 °C (13 Torr); ^1H NMR ($CDCl_3$): 0.964 (s, 9 H, Bu^t), 2.164 (s, 6 H, NMe_2), 3.074 (s, 1 H, α-CH), 7.15—7.25 (m, 5 H, Ph).

Synthesis of cyclopalladated complexes

Di-μ-chloro-bis[(*S*)-2-(1-dimethylamino-2,2-dimethylpropyl)phenyl-*C,N*]dipalladium(II) ((*S,S*)-2). Li_2PdCl_4 (3.3 g, 13 mmol) was placed in a three-neck flask and dissolved in anhydrous methanol (100 mL) in an atmosphere of argon. The solution was cooled to 2 °C, and (*S*)-*N,N*-dimethyl-α-*tert*-butylbenzylamine (2.48 g, 13 mmol) with an optical purity of 92% *ee* and excess AcONa (1.69 g, 20.6 mmol) were added. The reaction mixture was stirred at the same temperature for 8 h in an atmosphere of argon, with monitoring by TLC (Silufol, benzene/acetone 7 : 1). The precipitate that formed was filtered off and washed with methanol. The complex was extracted with chloroform on a filter separating it from palladium black (0.067 g, 0.6 mmol, 4.8%). After concentrating the organic extract to 7 mL, the dimeric complex was precipitated with hexane to obtain complex (*S,S*)-**2** (3.465 g). AcONa (0.323 g, 3.9 mmol) was added to the main methanolic mother liquor; after 4 days at −2 °C, an additional amount of dimer (*S,S*)-**2** (0.496 g) was isolated by column chromatography (Silpearl, *d* 2.5 cm, *h* 14 cm, benzene as eluent); the overall yield was 78% (81% if regenerated Pd^0 was taken into account). After recrystallization of combined portions of the dimer from a chloroform—hexane system, the optically pure dimer (*S,S*)-**2** (3.75 g) was obtained. It was then dried *in vacuo* (1 Torr) over $CaCl_2$ and paraffin, m.p. (with decomp.) 184—188 °C; $[\alpha]_D$ +255° (*c* 0.4, chloroform); R_f 0.91 (Silufol, benzene—acetone 5 : 1). Found (%): C, 47.2; H, 6.2; N, 4.2. $C_{26}H_{40}Cl_2N_2Pd_2$. Calculated (%): 47.1; H, 6.0; N, 4.2.

Determination of the optical purity of di-μ-chloro-bis[(*S*)-2-(1-dimethylamino-2,2-dimethylpropyl)phenyl-*C,N*]dipalladium(II) ((*S,S*)-2), by ^1H NMR

1. **Generation of a 1 : 1 mixture of diastereomers (*S,S*)-5a/(*R,S*)-5b *in situ*.** Two drops of (*S*)-α-methylbenzylamine were added to a solution of racemic dimer (*RR,SS*)-**2** (0.0217 g, 0.033 mmol) in $CDCl_3$ (0.5 mL). The obtained reaction mixture was used for recording the ^1H NMR spectrum, which contained three series of signals in a ratio of 1 : 1 : 4 corresponding to the two diastereomeric adducts ((*S,S*)-**5a** and (*R,S*)-**5b**) and free (*S*)-α-methylbenzylamine, respectively (see Table 1).

2. **Determination of the optical purity of dimer (*S,S*)-2.** Similarly to the previous procedure, a solution of recrystallized dimer (*S,S*)-**2** (0.0217 g, 0.033 mmol) in $CDCl_3$ (0.5 mL) was treated with (*S*)-α-methylbenzylamine (0.0317 g, 0.261 mmol). The ^1H NMR spectrum of complex (*S,S*)-**5a** formed *in situ* (see Table 1) contains only the signals corresponding to the one diastereomer (*S,S*)-**5a** and free (*S*)-α-methylbenzylamine in a ratio of 1 : 3.

Chloro[(*S*)-2-(1-dimethylamino-2,2-dimethylpropyl)phenyl-*C,N*][(*S*)-1-methylbenzylamine-*N*]palladium(II) ((*S,S*)-5a). Dimeric complex (*S,S*)-**2** (0.1017 g, 0.153 mmol) was placed in a flask filled with argon, and (*S*)-α-methylbenzylamine (0.1483 g, 1.224 mmol) and chloroform (5 mL) were added. The reaction mixture was stirred for 10 min and concentrated to a volume of 1 mL, and heptane was added until the beginning of crystallization. Two hours later the crystals were filtered off, washed with heptane, and dried *in vacuo* (1 Torr) over $CaCl_2$ and paraffin. The complex (0.1052 g, 76%) was obtained as colorless lamellar crystals, m.p. (with decomp.) 101—104 °C; $[\alpha]_D$ 140° (*c* 0.4, chloroform). Found (%): C, 56.0; H, 7.1; N, 5.8. $C_{21}H_{31}ClN_2Pd$. Calculated (%): C, 55.6; H, 6.8; N, 6.2.

Chloro[(*S*)-2-(1-dimethylamino-2,2-dimethylpropyl)phenyl-*C,N*](pyridine-*N*)-palladium(II) ((*S*)-6). Pyridine (0.0612 g, 77.4 mmol) was added to a solution of dimer (*S,S*)-**2** (0.1467 g, 0.221 mmol) in absolute benzene (10 mL). The reaction mix-

ture was stirred for 1 h at ~20 °C in an argon flow and concentrated to a volume of 2 mL, and heptane was added until the beginning of crystallization. The colorless crystalline complex (*S*)-**6** (0.1304 g, 72%) was obtained, m.p. (with decomp.) 157—162 °C; $[\alpha]_D$ +270° (*c* 0.4, chloroform). Found (%): C, 52.3; H, 5.9; N, 6.7. $C_{18}H_{25}ClN_2Pd$. Calculated (%): C, 52.6; H, 6.1; N, 6.8.

Chloro[(*S*)-2-(1-dimethylamino-2,2-dimethylmethylpropyl)phenyl-*C*,*N*](triphenylphosphine-P)palladium(II) ((*S*)-7). Triphenylphosphine (0.0800 g, 0.305 mmol) was added to a solution of dimer (*S*,*S*)-**2** (0.1001 g, 0.151 mmol) in absolute benzene (7 mL), and the mixture was stirred for 1 h in an argon flow. The reaction mixture was filtered and concentrated to a volume of 1 mL, and heptane was added until the beginning of crystallization. Complex (*S*)-**7** (0.1491 g, 83%) was obtained as pale yellow crystals, m.p. (with decomp.) 225—230 °C; R_f (Silufol, benzene/acetone 5 : 1) 0.55; $[\alpha]_D$ +120° (*c* 0.4, chloroform). Found (%): C, 62.6; H, 6.1; N, 2.1. $C_{31}H_{35}ClNPPd$. Calculated (%): C, 62.6; H, 5.9; N, 2.4.

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