

## Enantiomeric Discrimination in the Complexation of Ortho-palladated $\alpha$ -Arylalkylamines with the Racemic *tert*-Butylmethylphenylphosphine.

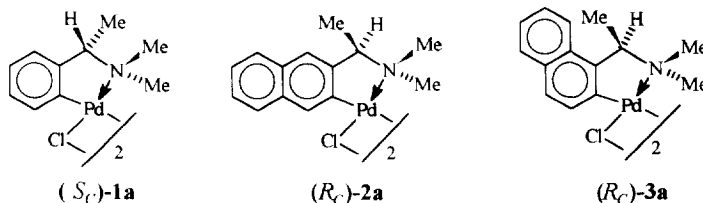
V.V.Dunina\*, E.B.Golovan', N.S.Gulyukina, A.V.Buyevich

Department of Chemistry, M.V.Lomonosov Moscow State University, 119899, V-234,  
Moscow, Russia., Fax: +7 (095) 932-88-46.

**Abstract.** A high degree of diastereoselectivity was achieved in the coordination of monodentate phosphine  $\text{PMeBu}^t\text{Ph}$  with dimeric chloro-bridged ortho-palladated complexes in solution due to the modification of the stereoselector structure, namely by the creation of asymmetry in the environment of nitrogen donor atom and by the fitting of substituents sizes in the palladacycle. The stereochemistry of complexation is discussed in the terms of equilibrium constants between two diastereomers of monophosphine complexes estimated from the  $^{31}\text{P}$  NMR data.

### INTRODUCTION

In spite of the successful resolution of diverse ligands by means of homochiral cyclopalladated compounds only three such complexes (**1a-3a**)<sup>1</sup> or their derivatives<sup>2</sup> were used until now as the resolving agents.



All these complexes contain  $\alpha$ -C\*-stereocentre as the sole chirality source. As a rule they are really employed as chiral derivatizing agents in reaction of 1:1 (substrate/Pd) stoichiometry; the resolution is achieved due to the different solubility of two diastereomeric adducts. Only in some instances was diastereoselectivity detected in the formation of mononuclear<sup>3</sup> or more sterically crowded binuclear adducts<sup>4</sup> with bidentate ligands in solution.

When we started our investigations in this area<sup>5,6</sup> only two publications<sup>7,8</sup> dealing with the monodentate phosphines resolution with the optically active complexes **1a** or **2a** were known. These experiments were performed under conditions allowing the preferential selection of one of two enantiomers of substrate (phosphine/palladium ratio was 2:1). Nevertheless authors<sup>7</sup> have concluded that "the present systems lack a

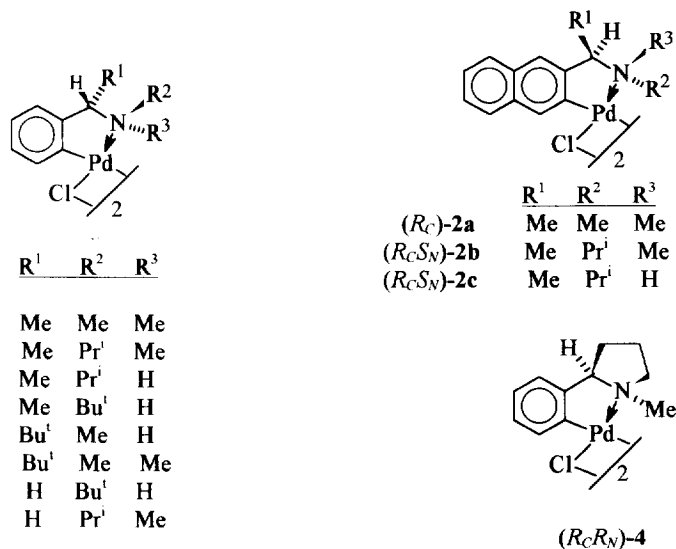
chiral recognition ability in solution<sup>7</sup>; the selective precipitation of one of two diastereomeric monophosphine adducts in some cases was assumed to be a result only of their solubility difference.

Recently there were published three more articles devoted to the resolution of monodentate P-containing ligands, namely atropisomeric dinaphthophosphine<sup>9</sup> and phosphole<sup>10,11</sup>, with the (*S<sub>C</sub>*)- or (*R<sub>C</sub>*)-**1a** reagent. To note, whilst Tani<sup>11</sup> have described the reaction of (*S<sub>C</sub>*)-**1a** with the fluxional phosphole as the stereoselective one, unfortunately, it's not evident from the <sup>1</sup>H NMR data presented<sup>12</sup>. The systematic investigations of stereochemistry of cyclopalladated compounds complexation with racemic ligands have not been carried out until now.

The main goal of the present work was to elucidate partly the factors governing the stereochemical course of monodentate phosphine complexation with ortho-palladated complexes. To answer this question we have modified the structure of these complexes using as the most important structural variables the presence or the absence of an asymmetric nitrogen atom in the palladacycle and the sterical demanding of α-C\*- and/or N\*-substituents.

## RESULTS

**Objects.** For the stereoselectors we have used a series of the ortho-palladated complexes containing stereogenic α-benzylic and nitrogen centres (**1b-e**, **2b,c**, **4**) derived from unsymmetrically N-substituted α-arylalkylamines.

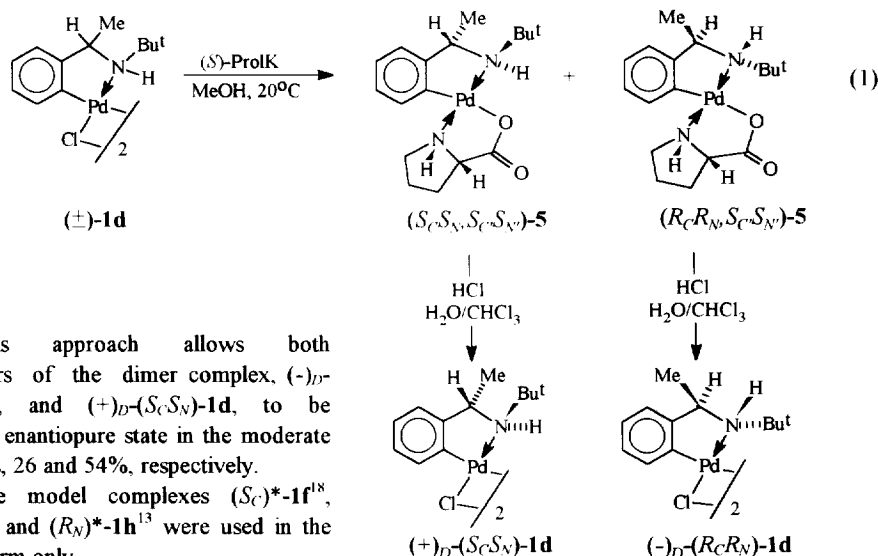


Unlike the known complexes **1a-3a** differing in the nature of aryl group only, the new potential stereoselectors differ in the nature of N-donor atom (secondary or tertiary), in the volume of α-C\*- and/or N\*-substituents (H, Me, Pr<sup>i</sup>, Bu<sup>i</sup>), and in the relationship between the absolute configurations of two adjacent stereocentres (the same or opposite). Several model complexes containing only one of two possible stereogenic atoms, either α-C\* (**1a,f**, **2a**) or N\* (**1g,h**), were used to estimate the role played by each of these chirality sources in the stereocontrol of phosphine bonding.

As the test racemic substrate for the comparison of the chiral recognition ability of these complexes we chose the *tert*-butylmethylphenylphosphine (**P\***). This ligand is monodentate and capable to rapid exchange

between coordinated and free states (that is required for the enantioselection under thermodynamic control) and contains two alkyl groups (Me and Bu<sup>t</sup>) of differing size yet convenient for spectroscopic analysis.

**Preparation of dimeric complexes.** The homochiral dimeric complexes (*S<sub>C</sub>R<sub>N</sub>*)-**1b**,<sup>c</sup><sup>13,14</sup>, (*R<sub>C</sub>S<sub>N</sub>*)-**2b**,<sup>c</sup><sup>15</sup> were obtained from the corresponding optically active amines as described previously. The synthesis of the racemic complexes (*S<sub>C</sub>S<sub>N</sub>*)\*-**1d**<sup>16</sup>, (*S<sub>C</sub>R<sub>N</sub>*)\*-**1e**<sup>16</sup> and (*R<sub>C</sub>R<sub>N</sub>*)\*-**4**<sup>17</sup> and optical resolution of two last-named racemates were published recently. Here we have performed the optical resolution of the racemic dimer (*S<sub>C</sub>S<sub>N</sub>*)\*-**1d** using the same methodology, based on the use of the solubility difference between two its (*S*)-prolinate derivatives, (*S<sub>C</sub>S<sub>N</sub>*,*S<sub>C</sub>S<sub>N</sub>*)-**5** and (*R<sub>C</sub>R<sub>N</sub>*,*S<sub>C</sub>S<sub>N</sub>*)-**5**.



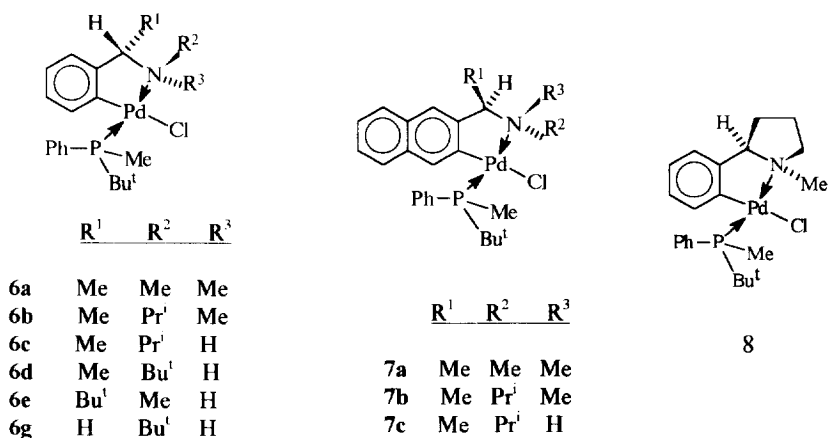
This approach allows both enantiomers of the dimer complex, (-)-*D*-(*R<sub>C</sub>R<sub>N</sub>*)-**1d**, and (+)-*D*-(*S<sub>C</sub>S<sub>N</sub>*)-**1d**, to be isolated in enantiopure state in the moderate total yields, 26 and 54%, respectively.

The model complexes (*S<sub>C</sub>*)\*-**1f**<sup>18</sup>, (*S<sub>N</sub>*)\*-**1g**<sup>19</sup> and (*R<sub>N</sub>*)\*-**1h**<sup>13</sup> were used in the racemic form only.

**The stereochemistry of dimeric complexes** (*S<sub>C</sub>R<sub>N</sub>*)-**1b**,<sup>c</sup>,<sup>e</sup> and (*R<sub>C</sub>S<sub>N</sub>*)-**2b**,<sup>c</sup> was established previously by means of <sup>1</sup>H NMR and CD spectroscopy<sup>13-16</sup>, using X-ray structure investigation of certain of these dimeric complexes or their mononuclear derivatives<sup>20</sup> as a basis for the assignments. We have shown that the ortho-palladation of  $\alpha$ -C\*-chiral tertiary  $\alpha$ -arylalkylamines bearing two different N-substituents<sup>13,15</sup> and of the most of secondary amines<sup>14</sup> is a stereospecific process. A peculiarity of the complexes of the stereochemical C\*N\*-type is that the stereogenic nitrogen centre adopts the configuration which is opposite to that of the adjacent  $\alpha$ -benzylic carbon stereocentre. Such a relative configuration results from the striving of more bulky N\*-substituent for the transoid disposition relative to the  $\alpha$ -C\* substituent to decrease the sterical strain in the palladacycle. The configurational stability of the stereogenic nitrogen atom is supported by the adjacent carbon centre.

Based on the same reasoning, using <sup>1</sup>H NMR data<sup>16</sup> and comparing the [ $\alpha$ ]<sub>D</sub> sign of (-)-**1d** and (+)-*D*-**1d** enantiomers with that of known dimer complexes (*S<sub>C</sub>R<sub>N</sub>*)-**1b**,<sup>c</sup>,<sup>e</sup> and (*R<sub>C</sub>S<sub>N</sub>*)-**2b**,<sup>c</sup><sup>13-16</sup> we have assigned to them tentatively the same transoid stereochemistry, namely (-)-*D*-(*R<sub>C</sub>R<sub>N</sub>*)-**1d** and (+)-*D*-(*S<sub>C</sub>S<sub>N</sub>*)-**1d**. To note, the difference in the description of the configuration of **1d** enantiomers and that of the remaining complexes **1**, **2** arises from the change in the N-substituents priorities only. The absolute configuration of (*R<sub>C</sub>R<sub>N</sub>*)-**4** complex was established by X-ray structure investigation of its (*S*)-prolinate derivative<sup>21</sup>; the tentative assignment made previously on the base of CD data was erroneous<sup>17</sup>.

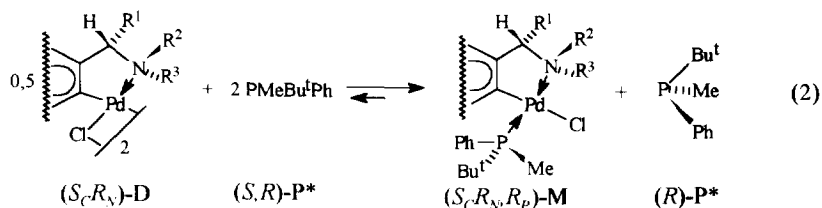
The isolation of monophosphine adducts (6-8) was undertaken for the subsequent spectral identification of species forming during the complexation of dimeric complexes 1, 2, 4 with phosphine P\* in solution. The enantiomerically pure diastereomers (either both or one only) of complexes 6a-c, 7a-c were obtained previously<sup>5</sup>. Here we have performed the chromatographic separation of adduct 8 isomers, resulted in the isolation of enantiomerically pure ( $R_C R_N, R_P$ )-8 diastereomer whereas the second isomer ( $R_C R_N, S_P$ )-8 was obtained in the enriched form only (80% *de*). All our attempts to separate two diastereomers of complex 6e and two diastereomeric racemates of adduct 6d have been unsuccessful due to their close solubility and chromatographic mobility. After chromatographic purification (without diastereomers separation) we have obtained a highly enriched diastereomer ( $S_C R_N, R_P$ )-6e (83% *de*), and diastereomeric racemate ( $S_C S_N, R_P$ )\*-6d (80% *de*).



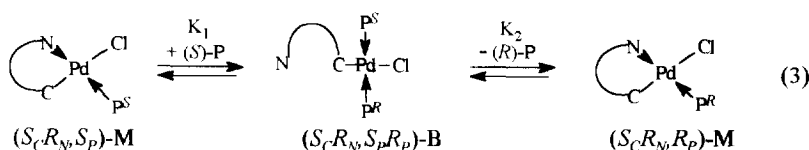
We didn't attempt to separate the two diastereomeric racemates of model complex 6g containing only a N\*-stereocentre in the palladacycle. Its configurational lability is quite evident from the change of ( $S_N, R_P$ )\*/( $S_N, S_P$ )\* diastereomeric racemates ratio in the isolated complex 6g depending on the temperature: from 5:1 ratio at room temperature up to 12:1 ratio at -60°C (see exp.).

The absolute configuration of complexes 6a-c, 7a-c and 8 isolated was estimated on the base of CD spectra of the individual diastereomers and their 1:1 mixtures; X-ray structure investigation of ( $S_C R_N, R_P$ )-6b, and ( $R_C S_N, S_P$ )-7b adducts was used as a basis for the assignments<sup>22</sup>. The relative configuration of stereocentres in diastereomeric racemates ( $S_C S_N, R_P$ )\*-6d, ( $S_C R_N, R_P$ )\*-6e, and ( $S_N, R_P$ )\*-6g was assigned tentatively on the base of <sup>1</sup>H NMR data only.

**The stereochemistry of P\* bonding in solution.** The interaction of homochiral dimeric ortho-palladated complexes (D) with the stoichiometric amount of the racemic monodentate phosphine (P\*/Pd ratio 1:1) have to result in the formation of the equimolar mixture of two possible diastereomeric monophosphine adducts (M) provided that the phosphine ligand is a configurationally stable molecule (cf. <sup>11</sup>). The use of a twofold excess of racemic P\* (P\*/Pd ratio ca. 2) offers the possibility of the selection between two its enantiomers. Taking into account the known kinetic lability of Pd(II) complexes this process seems to be thermodynamically controlled. Ideally, only one enantiomer of P\* may be bound in the chiral complex leaving the other enantiomer uncoordinated as it is illustrated below (eq. 2) for the ( $S_C R_N$ )-D/P\* system.



It is reasonably to suppose that in the presence of excess phosphine the equilibrium between the two diastereomers of the monophosphine adducts M is attained through the isomeric bisphosphine adducts B formation and dissociation (eq. 3) rather than *via* the dimer D regeneration (eq. 2). The tendency of cyclopalladated complexes to dechelate in the presence of phosphine excess is well known<sup>23</sup>.



The complicated composition of the reaction mixtures formed and fast phosphine P\* exchange between M and B species in solution has required to use low-temperature <sup>31</sup>P NMR spectra (188 $\pm$ 5 K) for their investigation. In the general case spectral data obtained show the presence of two diastereomeric monophosphine adducts M ( $\delta$  33.5-38.5 ppm), several isomeric *trans*-bis-phosphine complexes B ( $\delta$  8-20 ppm, up to 4 species) and unreacted phosphine ( $\delta$  ca. -12 ppm).

As the most suitable quantitative measure of the diastereoselectivity of the phosphine P\* bonding we have chosen the equilibrium constant (K) between the two diastereomers of monophosphine adduct (according to eq. 3). In all cases we considered the formation of the predominant diastereomer from minor one ( $K > 1$ ). For example, in the instances of C\*N\*-stereoselectors we have employed the equation (4):

$$K = K_1 \cdot K_2 = \frac{[(S_C R_N, R_P)\text{-M}] [(R)\text{-P}]}{[(S_C R_N, S_P)\text{-M}] [(S)\text{-P}]} \quad (4)$$

where  $[(S_C R_N, R_P)\text{-M}]$  and  $[(S_C R_N, S_P)\text{-M}]$  denote the concentrations of dominant and minor diastereomers of the monophosphine adduct, and  $[(R)\text{-P}]$  and  $[(S)\text{-P}]$  that of two enantiomers of the free phosphine. Stereochemical identification of two diastereomers M signals observed in the <sup>31</sup>P NMR spectra of D/P\* solutions was carried out on the base of spectral data of isolated individual diastereomers of monophosphine adducts and their mixtures of various compositions both at room and lowered temperatures.

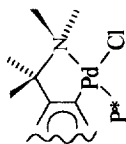
The use of racemic phosphine ligand in reactions investigated allows the  $[(R)\text{-P}]$  and  $[(S)\text{-P}]$  concentrations to be expressed in the general case as follows:

$$[(R)\text{-P}] = 0.5 [P] + 0.5\Delta[M] + \Delta[B'] \quad (5)$$

$$[(S)\text{-P}] = 0.5 [P] - 0.5\Delta[M] - \Delta[B'] \quad (6)$$

where [P] denotes the total concentration of the free phosphine, and  $\Delta[M]$  and  $\Delta[B']$  designate the difference between the concentrations of dominant ( $S_C R_N, R_P$ )- and minor ( $S_C R_N, S_P$ )- diastereomers of monophosphine

Table 1. The Study of Selectivity of Methyl-*tert*-butylphosphine Bonding with Chiral Palladacycles by  $^{31}\text{P}$  NMR Spectroscopy ( $\text{CD}_2\text{Cl}_2$ , 188 K).



En-try	Starting dimer <b>D</b>	Side chain	Ar	P*/Pd ratio	B (mol%)	Diastereomeric monophosphine complexes			Constant K
						dominant form	chem. shift ( $\delta$ , ppm)	isomers ratio	
1	( <i>S<sub>C</sub></i> )- <b>1a</b>		Ph	2.0 <sup>3)</sup>	69	( <i>S<sub>C</sub>S<sub>P</sub></i> )- <b>6a</b>	37.24; 36.33	5.4 : 1	-
2	( <i>S<sub>C</sub></i> )*- <b>1a</b>		Ph	1.1	6	( <i>S<sub>C</sub></i> )*- <b>6a</b>	37.26; 36.37	3.0 : 1	3.0
3	( <i>S<sub>C</sub>R<sub>N</sub></i> )- <b>1b</b>		Ph	2.1	63	( <i>S<sub>C</sub>R<sub>N</sub>R<sub>P</sub></i> )- <b>6b</b>	36.10; 35.64	23 : 1	-
4	( <i>S<sub>C</sub>R<sub>N</sub></i> )*- <b>1b</b>		Ph	1.1	7	( <i>S<sub>C</sub>R<sub>N</sub>R<sub>P</sub></i> )*- <b>6b</b>	36.11; 35.66	6.2 : 1	6.2
5	( <i>S<sub>C</sub>R<sub>N</sub></i> )- <b>1c</b>		Ph	2.15	14	( <i>S<sub>C</sub>R<sub>N</sub>R<sub>P</sub></i> )- <b>6c</b>	36.82; 36.67	6:1	24 (16-29)
6	( <i>S<sub>C</sub>R<sub>N</sub></i> )*- <b>1c</b>		Ph	1.1	0	( <i>S<sub>C</sub>R<sub>N</sub>R<sub>P</sub></i> )*- <b>6c</b>	36.81; 36.72	15.7 : 1	15.7
7	( <i>S<sub>C</sub>S<sub>N</sub></i> )- <b>1d</b>		Ph	1.9	4	( <i>S<sub>C</sub>S<sub>N</sub>R<sub>P</sub></i> )- <b>6d</b>	37.64; 36.84	1 : 2.4	6.3 (5.8-6.7)
8	( <i>S<sub>C</sub>S<sub>N</sub></i> )*- <b>1d</b>		Ph	1.1	1	( <i>S<sub>C</sub>S<sub>N</sub>R<sub>P</sub></i> )*- <b>6d</b>	37.64; 36.84	1 : 4.2	4.2
9				1.1	1		37.65; 36.84	1 : 4.8	4.8
10				1.1	1		37.66; 36.85	1 : 4.5	4.5

11	$(S_C R_N)$ -1e		Ph	1.8	0	$(S_C R_N, R_P)$ -6e	38.42; 35.52	2.5 : 1	8.4
12	$(S_C)$ *-1f		Ph	1.1	0.3	6f <sup>(5)</sup>	35.08; 33.59	9.0 : 1	9.0
13 14	$(S_N)$ *-1g		Ph	1.7 1.1	71 9	$(S_N, R_P)$ *-6g	37.46; 36.74 37.37; 36.62	1 : 18.7 1 : 11.5	- 11.5
15 16	$(R_N)$ *-1h		Ph	1.6 1.05	58 4	6h <sup>(5)</sup>	36.42; 36.35 36.42; 36.37	2.0 : 1 1.4 : 1	- 1.4
17	$(R_C)$ -2a		$\beta$ -Np	2.15	82	$(R_C, R_P)$ -7a	37.60; 36.68	4.2 : 1	-
18	$(R_C S_N)$ -2b		$\beta$ -Np	1.7 <sup>(4)</sup>	31	$(R_C, S_N, S_P)$ -7b	36.15; 35.74	3.1 : 1	-
19 20	$(R_C S_N)$ -2c		$\beta$ -Np	1.8 1.8	23 23	$(R_C, S_N, S_P)$ -7c	37.21; 36.70 37.21; 36.70	6.3 : 1 6.3 : 1	(>30)
21 22	$(R_C R_N)$ -4 $(R_C R_N)$ *-4		Ph	2.05 1.1 <sup>(3)</sup>	77 9	$(R_C R_N, R_P)$ -8 $(R_C R_N, R_P)$ *-8	37.57; 36.49 37.65; 36.52	5.7 : 1 4.1 : 1	- 4.1

<sup>1)</sup> molar proportion of all bisphosphine complexes of the total content of Pd(II) containing species; <sup>2)</sup> equilibrium constant  $K$ , values were calculated for the formation of dominant diastereomer from the minor one ( $K > 1$ ) without considering of bisphosphine complexes; the range of  $K$  variation depending on the B composition are given in brackets; <sup>3)</sup> the spectra was recorded at 185 K; <sup>4)</sup> this experiment was performed using Schlenk technique and the spectra was registered on a Varian FT-80A spectrometer (32.2 MHz) at the temperature 198 K; <sup>5)</sup> the configuration of diastereomeric monophosphine complexes is not known;

complex M and that between the ( $S_C R_N, R_P, R_P$ )- and ( $S_C R_N, S_P, S_P$ )-diastereomers of bisphosphine complex B, respectively.

However, due to the uncertainty in the distribution of two enantiomers of P\* among the isomeric bisphosphine complexes the determination of [(*R*)-P] and [(*S*)-P] values can be made sufficiently fair only in the absence of detectable amounts of species B in the solution (1d,e/P\* systems, entry 7, 11 in tabl. 1). Our estimation of the limits of equilibrium constant values variation depending upon the assumption that either ( $S_C R_N, R_P, R_P$ )-B or ( $S_C R_N, S_P, S_P$ )-B diastereomer is a predominant species in the systems with moderate B content has shown the twofold (K 16-29 for 1c, entry 5) or more wide alteration of K values (from 30 up to infinity for 2c, entry 19). Finally, when dechelation extent is increased up to the 63-82% (entry 1, 3, 17, 21) the constant K estimation becomes impossible at all and only the ratio of two diastereomeric monophosphine adducts M can be used as a qualitative measure of the reaction selectivity.

To overcome these complications we have replaced the homochiral complexes D by the racemic one and have decreased the excess of P\* substrate down to 10 mol% (P\*/Pd ratio of ca. 1.1:1). The same regime was used for the model complexes 1g,h containing the sole N\*-stereocentre because of they are inaccessible in the homochiral state. For such systems the estimation of the equilibrium constant K value is simplified due to the equal concentrations of (*R*)- and (*S*)-enantiomers of the uncoordinated phosphine P\* in the reaction mixture (see eq. 4). As the result constant K value becomes identical to the ( $S_C R_N, R_P$ )\*-M and ( $S_C R_N, S_P$ )\*-M diastereomers ratio (eq. 7).

$$K = \frac{[(S_C R_N, R_P)^* \text{-M}]}{[(S_C R_N, S_P)^* \text{-M}]} \quad (7)$$

Since this most simple expression (eq. 7) do not require the calculation of free (*R*)-P\* and (*S*)-P\* enantiomer concentrations it guarantees more exactness in the determination of constant K values. Consequently, during the discussion of data obtained we employed mainly the K values which were obtained from the experiments with the racemic complexes D.

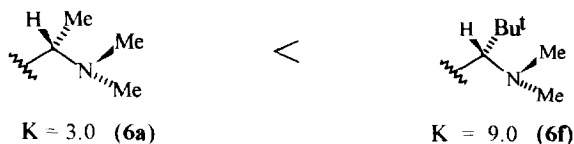
The fast attainment of the equilibrium state at low temperature (188 K) for the both regimes used was confirmed as follows. The sample of the reaction mixture ( $R_C S_N$ )-2c/P\* in ca. 1:4 ratio was prepared at the temperature 210 K and its NMR spectra was recorded at 188 K (entry 19); then the same sample was kept at room temperature for 0.5 h and the spectra was registered at 188 K once more (entry 20). The spectral pattern of the both samples were identical completely. For the system ( $S_C S_N$ )\*-1d/P\* in the ratio ca. 1:2.2 the same conclusion resulted from the invariability of spectral characteristics of the sample prepared under standard conditions (entry 8) after its storing for 17 h at 190 K (entry 9), and then for ca. 2 months at the temperature 280 K (entry 10).

## DISCUSSION

The most important result of this work is the discovery of marked enantioselectivity of phosphine P\* bonding by the most of complexes used. A rather wide variation of equilibrium constant K values (from 1.4 up to >30) depending upon chiral matrix structures allows some assumptions of the factors determining the selectivity level to be made.

First of all, the presence of only one  $\alpha$ -benzylic stereogenic carbon centre in the palladacycle of known complexes 1a, 2a was found to be sufficient to make one enantiomer P\* bonding some more preferable as compared to another: the K value ca. 3.0 was found in the case of ( $S_C$ )\*-1a/P\* system; the ( $S_C, S_P$ )-6a/( $S_C, R_P$ )-6a and ( $R_C, R_P$ )-7a/( $R_C, S_P$ )-7a diastereomer ratios were found to be equal ca. 5:1 and 4:1, respectively (67 and 60% *de*). Furthermore, the selectors of stereochemical C\*-type were somewhat improved due to the increasing of steric demands of  $\alpha$ -C\* substituent<sup>24</sup>: after the replacement of  $\alpha$ -Me group in the dimer ( $S_C$ )\*-1a by the more bulky  $\alpha$ -Bu<sup>t</sup> group in ( $S_C$ )\*-1f analogue the equilibrium constant K value increases from 3 up to 9.





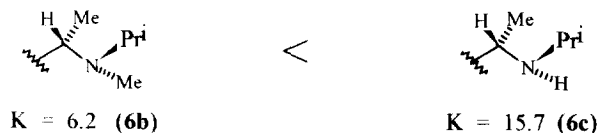
In such systems the more preferable bonding occurs with the very enantiomer of P\* phosphine having in the coordinated state the same absolute configuration as that of  $\alpha$ -C\* centre in the stereoselector ( $S_C$ )-1a and ( $R_C$ )-2a.

As the most essential structural modification of the known chiral complexes 1a, 2a we have introduced an asymmetric donor stereocentre in palladacycle. From the comparison of the behavior of two related complexes ( $S_C$ )-1a (entry 2) and ( $S_C R_N$ )-1b (entry 4) two consequences of N\*-asymmetry appearance can be seen:

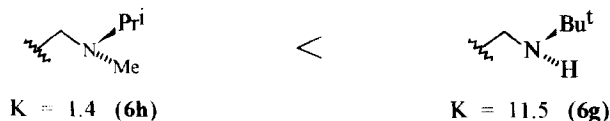
1) *The reversal of selectivity sign*: instead of the ( $S_C, S_P$ )-diastereomer of monophosphine complex prevailing in the 6a adduct composition, the more favoured diastereomer of 6b have the ( $S_C R_N, R_P$ )-configuration. The same is true as well for the ( $R_C S_N$ )-2b/P\* system, where the diastereomer ( $R_C S_N, S_P$ )-7b was found to be the dominant form: ( $R_C S_N, S_P$ )-7b/( $R_C S_N, R_P$ )-7b diastereomers ratio equal ca. 3:1 (entry 18). So, it is evident, that in (C\*N\*)-D/P\* systems the selection of the more favourable enantiomer of the phosphine ligand is dictated by the sterical requirements of just the N\*-stereocentre, despite of the opposite demands of the adjacent  $\alpha$ -benzylic stereocentre.

2) *A twofold enhancement of diastereoselectivity level* was found in the case of the C\*N\*-selector as compared to the C\*-model: the equilibrium constant K values are equal 3.0 and 6.2 for the ( $S_C$ )\*-1a/P\* and ( $S_C R_N$ )\*-1b/P\* systems, respectively.

To improve the chiral recognition ability of (C\*N\*)-type complexes we have increased the difference between the steric requirements of two N\*-substituents. The replacement of the tertiary NMePr<sup>i</sup> group in ( $S_C R_N$ )-1b with the secondary NHPr<sup>i</sup> group in ( $S_C R_N$ )-1c complex results in more than twofold increase of equilibrium constant K value, from 6.2 up to 15.7. The rough estimation of the equilibrium constant K value for the related  $\beta$ -naphthyl system ( $R_C S_N$ )-2c/P\* have shown that its value can be in the interval from 30 up to the infinity depending on the stereochemical composition of bisphosphine species (entry 19).



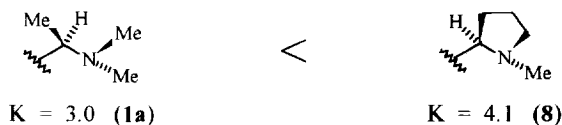
The most direct confirmation of the role played by the asymmetric donor nitrogen atom was obtained from the study of two model complexes ( $S_N$ )\*-1g and ( $R_N$ )\*-1h containing N\*-stereocenter as the sole chirality source. Both complexes display the diastereoselectivity in P\* coordination. But in these instances the "asymmetry extent" of N\*-donor centre environment appears to be especially important for their efficiency. So, the derivative of secondary benzylamine, ( $S_N$ )\*-1g is greatly superior to the ( $R_N$ )\*-1h analogue derived from the tertiary amine: constant K values are equal 11.5 and 1.4, respectively. The selectivity increase can be attributed to the greater difference between the volumes (and steric demands) of two N\*-substituents in the first case (NHBu<sup>t</sup> group) as compared to the second one (NMePr<sup>i</sup> group).



To note, by contrast with C\*N\*-type systems the model complexes ( $S_N$ )\*-1g and ( $R_N$ )\*-1h are not of practical significance on account of their configurational instability. In these instances the optimum combination of two chiral ligands stereochemistry is thought to be achieved not only due to the exchange of P\* enantiomers but also through the inversion of N\* centre configuration after its decoordination in bisphosphine species B. Nevertheless the high diastereoselectivity of the adduct 6g formation (K 11.5) can serve as a good argument in support of the existence of certain efficient steric interactions between N\* and P\* stereocenters despite their *trans*-arrangement within the palladium coordination sphere.

All complexes of C\*N\*-type discussed above were obtained from acyclic  $\alpha$ ,N-di- or  $\alpha$ ,N,N-trisubstituted arylmethylamines and contained two adjacent stereocentres in opposite configurations, namely ( $S_C R_N$ ) or ( $R_C S_N$ ). As was shown above, the requirements imposed by two chirality sources (C\* and N\*) upon the stereochemistry of the incoming phosphine ligand are opposite as well.

To overcome such "contradiction in interests" of two chirality sources in C\*N\*-systems we have used the ortho-palladated derivative of N-methyl-2-phenylpyrrolidine, ( $R_C R_N$ )-4, where the same configurations of  $\alpha$ -C\* and N\* atoms are fixed due to the sterical requirements of two fused five-membered cycles (that of pyrrolidine and palladacycle). This model complex was found to be some more selective in the complexation with racemic P\* as compared to the closely related N-achiral analogue ( $S_C$ )-1a: constant K values were found to be 4.1 and 3.0, respectively.



Despite the only modest difference, this result is in accordance with the concerted action of two chirality sources, namely ( $R$ )- $\alpha$ -C\*- and ( $R$ )-N\*-stereocentres. It seems reasonable to suppose that the reason of low contribution of N\*-stereocenter into the chiral recognition in the case of ( $R_C R_N$ )-4 is too small volumes difference between two N\*-substituents, formally N-CH<sub>2</sub>CH<sub>2</sub> and N-CH<sub>3</sub> groups.

## SUMMARY AND CONCLUSION

The most important result of the present work is a disclosure of highly efficient chiral discrimination in complexation of N\*-chiral ortho-palladated complexes with monodentate phosphine in solution. The derivatives of secondary  $\alpha$ -arylalkylamines containing a rather bulky N\*-substituent, namely isopropyl group, proved to be the most efficient stereoselectors. Such 1,3-chirality transfer from N\*-stereocentre onto the *trans*-disposed P\*-chiral phosphine ligand is seemed to be the rather surprising phenomenon. The reasons of chiral discrimination observed will be soon discussed separately on the base of NMR, CD data and X-ray structure characterization of certain of the monophosphine adducts<sup>22</sup>.

It seems important also that a high level of diastereoselectivity was achieved with the nearest analogues of ( $S$ )-N,N-dimethyl- $\alpha$ -methylbenzylamine based complex 1a which has shown itself to be a much worse resolving agent as compared to 1-(1-naphthyl)ethylamine derivative 3a. The factors responsible for the difference in the behavior of related complexes were considered recently<sup>25</sup>.

To our knowledge this is the first example of high diastereoselectivity in the coordination of a configurationally stable monodentate phosphine ligand with the optically active cyclopalladated compounds in solution. The selective bonding of P\*-chiral phosphines in solution creates a good starting conditions for their resolution by simple crystallization of monophosphine adducts. But it's especially important for the use of homochiral complexes of this type as the matrix in asymmetric transformations of coordinated ligands; the examples of such version of asymmetric synthesis are known now<sup>26</sup>.

## EXPERIMENTAL

**General.** Routine  $^1\text{H}$  NMR spectra were recorded at 400 MHz on a Varian VXR 400 instrument in  $\text{CDCl}_3$  at room temperature. Proton chemical shifts, reported in parts per million, were referenced to tetramethylsilane used as an internal standard. The  $^{31}\text{P}$  NMR spectra were registered at 81.0 MHz on a Bruker AC-200 spectrometer at  $188 \pm 5$  K using 85%  $\text{H}_3\text{PO}_4$  as an external standard. Specific rotations were measured on a VNIIEKI-Prod mush AI-EPO polarimeter in a 0.25-dm cell at  $20^\circ\text{C}$ .

All preparative synthesis were carried out under an atmosphere of argon. The solvents were dried and purified by standard methods<sup>27</sup>.

**tert-Butylmethylphenylphosphine** was prepared as described previously<sup>5</sup> and distributed among a series of thin-walled phials under vacuum.

**Potassium (*S*)-Prolinate** was obtained by interaction of equimolar quantities of (*S*)-proline (1.9271 g, 16.7 mmol) and KOH (0.9391 g, 16.7 mmol) in methanol (10 mL) under stirring for 10 min, with subsequent evaporation in vacuo and drying at  $80\text{--}90^\circ\text{C}$  ( $10^{-2}$  torr). Yield 2.2070 g (95%), m.p.  $210\text{--}215^\circ\text{C}$  (dec.).

### Resolution of $(\pm)$ -di- $\mu$ -chlorobis[2-{1-(*tert*-butylamino)ethyl}phenyl-C,N]-dipalladium(II) $(\pm)$ -1d.

(1). **Formation and separation of internal diastereomers of [(*R*<sub>C</sub>*R*<sub>N</sub>/*S*<sub>C</sub>*S*<sub>N</sub>)-2-{1-(*tert*-butylamino)ethyl}phenyl-C,N]] (*S*<sub>C</sub>*S*<sub>N</sub>)-prolinate-N,O]palladium(II), (*R*<sub>C</sub>*R*<sub>N</sub>,*S*<sub>C</sub>*S*<sub>N</sub>)-5 and (*S*<sub>C</sub>*S*<sub>N</sub>,*S*<sub>C</sub>*S*<sub>N</sub>)-5.** A solution of a slight excess of potassium (*S*)-prolinate (0.2362 g, 1.54 mmol) in anhydrous MeOH (20 mL) was added to a suspension of the racemic dimeric complex  $(\pm)$ -1d (0.4423 g, 0.695 mmol) in the same solvent (10 mL). After being stirred at room temperature for an hour, the mixture was filtered, the filtrate was reduced in vacuo to a solid. The product was extracted with dichloromethane ( $3 \times 10$  mL), the resultant solution was partially evaporated and slowly diluted with diethyl ether to give colorless crystals enriched in diastereomer (*R*<sub>C</sub>*R*<sub>N</sub>,*S*<sub>C</sub>*S*<sub>N</sub>)-5. Three subsequent recrystallizations from the same system ( $\text{CH}_2\text{Cl}_2/\text{Et}_2\text{O}$ ) afforded diastereomerically pure complex (*S*<sub>C</sub>*S*<sub>N</sub>,*S*<sub>C</sub>*S*<sub>N</sub>)-5  $0.5\text{Et}_2\text{O}$  as colorless crystals in 62% yield (0.1856 g): m.p.  $235\text{--}236^\circ\text{C}$  (dec.);  $[\alpha]_{\text{D}}^{20} +170$  (c 0.62, MeOH);  $R_f$  0.70 ( $\text{CHCl}_3/\text{EtOH}$  7:1).

$^1\text{H}$  NMR:  $\delta$  1.26 (s, 9H, Bu<sup>t</sup>), 1.75 (d,  $^3J_{\text{HH}}$  6.6 Hz, 3H, CHMe), 3.69 (br.s, 1H, NH), 4.13 (m, 1H,  $\alpha$ -CH), 6.83-6.97 (m, 4H, aromatics); prolinate:  $\delta$  1.69 (m, 1H), 1.98 (m, 1H), 2.31 (m, 2H), 3.28 (m, 2H), 4.13 (m, 1H), 4.40 (br.m, 1H, NH); Et<sub>2</sub>O:  $\delta$  1.21 (t, 3H, CH<sub>3</sub>), 3.48 (q, 2H, CH<sub>2</sub>). Anal. Calc.: C, 52.65; H, 7.17; N, 6.45 for  $\text{C}_{17}\text{H}_{26}\text{N}_2\text{O}_2\text{Pd} \cdot 0.5\text{Et}_2\text{O}$ . Found: C, 52.61; H, 6.97; N, 6.73.

The first mother liquor was partially evaporated and slowly diluted with hexane to give colorless crystals enriched in the another isomer of derivative 5; its four recrystallizations from  $\text{CH}_2\text{Cl}_2/\text{hexane}$  afforded pure (*R*<sub>C</sub>*R*<sub>N</sub>,*S*<sub>C</sub>*S*<sub>N</sub>)-5 diastereomer in 30% yield (0.0838 g): m.p.  $217\text{--}219^\circ\text{C}$  (dec.);  $[\alpha]_{\text{D}}^{20} +75$  (c 0.63, MeOH);  $R_f$  0.68 ( $\text{CHCl}_3/\text{EtOH}$  7:1).

$^1\text{H}$  NMR:  $\delta$  1.31 (s, 9H, Bu<sup>t</sup>), 1.66 (d,  $^3J_{\text{HH}}$  6.6 Hz, 3H, CHMe), 3.44 (br.s, 1H, NH), 4.13 (m, 1H,  $\alpha$ -CH), 6.76-6.96 (m, 4H, aromatics); prolinate (m, 1H):  $\delta$  1.72, 1.99, 2.17, 2.34, 3.38, 3.54, 3.68, 4.04.

### (2) Isolation of enantiopure dimeric complexes (+)<sub>D</sub>-(*S*<sub>C</sub>*S*<sub>N</sub>)-1d and (-)<sub>D</sub>-(*R*<sub>C</sub>*R*<sub>N</sub>)-1d.

The solution of pure diastereomer (*S*<sub>C</sub>*S*<sub>N</sub>,*S*<sub>C</sub>*S*<sub>N</sub>)-5  $0.5\text{Et}_2\text{O}$  (0.1856 g, 0.4278 mmol) in chloroform (10 mL) was shaken with equal volume of 1M HCl for 3 min. The organic layer was separated, washed with water, dried over  $\text{Na}_2\text{SO}_4$ , filtered and evaporated in vacuo. The residual moisture was then removed by its azeotropic distillation with benzene under reduced pressure. The crude product was finally recrystallized from dichloromethane/hexane system to give enantiomer (+)<sub>D</sub>-1d in 87% yield (0.1184 g): m.p.  $219\text{--}220^\circ\text{C}$  (dec.);  $[\alpha]_{\text{D}}^{20} +78$  (c 0.51,  $\text{CH}_2\text{Cl}_2$ );  $R_f$  0.31 ( $\text{C}_6\text{H}_6/\text{Me}_2\text{CO}$  25:1). Anal. Calc.: C, 45.30; H, 5.70; N, 4.40 for  $\text{C}_{24}\text{H}_{36}\text{Cl}_2\text{N}_2\text{Pd}_2$ . Found: C, 45.89; H, 5.50; N, 3.71.

Enantiomer (-)<sub>D</sub>-**1d** was isolated similarly from 0.0838 g (0.211 mmol) of pure diastereomer (*R<sub>C</sub>R<sub>N</sub>,S<sub>C</sub>S<sub>N</sub>*)-**5** in 86% yield (0.0578 g);  $[\alpha]_D^{20}$  -77 (c 0.49, CH<sub>2</sub>Cl<sub>2</sub>); m.p. 219-220°C (dec.).

#### The isolation of monophosphine adducts.

The synthesis and isolation of pure diastereomers of complexes **6a-c**, **7a-c** was described previously<sup>5</sup>.

**Chloro{2-[1-(*tert*-butylamino)ethyl]phenyl-C,N}{*tert*-butylmethylphenylphosphine-P}-palladium(II), (*S<sub>C</sub>S<sub>N</sub>,R<sub>P</sub>*)\*/(*S<sub>C</sub>S<sub>N</sub>,S<sub>P</sub>*)\*-**6d**.** The mixture of racemic dimer (*S<sub>C</sub>S<sub>N</sub>*)\*-**1d** (0.1894 g, 0.3 mmol) and 7 mL of 0.1M solution of racemic phosphine **P\*** (0.7 mmol) in CH<sub>2</sub>Cl<sub>2</sub> was stirred under argon for 0.5 h at r. t. and evaporated to dryness. After the chromatographic purification on the several flash columns (Silpearl, *h* 13.5 cm, *d* 1.8 cm) using the ether/pentane 2:1 mixture as an eluent and recrystallization from benzene/pentane 0.1367 g (46% yield) of the complex **6d** was obtained as a mixture of (*S<sub>C</sub>S<sub>N</sub>,R<sub>P</sub>*)\*/(*S<sub>C</sub>S<sub>N</sub>,S<sub>P</sub>*)\* diastereomeric racemates in the 9:1 ratio (<sup>1</sup>H NMR data) as the large light-yellow crystals: m.p. 160-161°C, *R<sub>f</sub>* 0,68 (Silufol UV-254, ether/pentane 2:1) for both diastereomers. Anal. Calc.: C, 55.43; H, 7.08; N, 2.81 for C<sub>23</sub>H<sub>35</sub>ClNPd. Found: C, 55.72; H, 7.26; N, 2.58.

<sup>31</sup>P NMR (CH<sub>2</sub>Cl<sub>2</sub>, r. t.): δ 36.78, 37.3 ppm; <sup>1</sup>H NMR (two sets of signals in 9:1 ratio): major isomer: δ 1.22 (s, 9H, NBU<sup>1</sup>), 1.31 (d, <sup>3</sup>J<sub>PH</sub> 15.0 Hz, 9H, PBU<sup>1</sup>), 1.62 (d, <sup>2</sup>J<sub>PH</sub> 8.6 Hz, 3H, PMe); 1.97 (d, <sup>3</sup>J<sub>HH</sub> 6.75 Hz, 3H, α-Me), 3.75 (br.m, 1H, NH), 4.13 (dq, 1H, α-CH); aromatics: δ 6.05 (m, 1H, C<sup>6</sup>H), 6.51 (dt, <sup>3</sup>J<sub>HH</sub> 7.5 Hz, <sup>4</sup>J<sub>HH</sub> 1.5 Hz, 1H, C<sup>5</sup>H), 6.82 (m, 2H, C<sup>4</sup>H + C<sup>3</sup>H); 7.48 (m, 3H, PPh), 8.00 (m, 2H, PPh); minor isomer: δ 1.24 (s, 9H, NBU<sup>1</sup>), 1.35 (d, <sup>3</sup>J<sub>PH</sub> 15.0 Hz, 9H, PBU<sup>1</sup>), 1.94 (d, <sup>3</sup>J<sub>HH</sub> 6.75 Hz, 3H, α-Me); aromatics: δ 6.14 (m, 1H, C<sup>6</sup>H), 6.39 (dt, <sup>3</sup>J<sub>HH</sub> 7.6 Hz, 1H, C<sup>5</sup>H), 6.74 (dt, <sup>3</sup>J<sub>HH</sub> 7.3 Hz, 1H, C<sup>4</sup>H or C<sup>3</sup>H); 7.36 (m, 3H, PPh); 7.83 (m, 2H, PPh); the signals of NH, α-CH, PMe and remaining aromatic protons are hidden under the more intensive signals of major isomer.

**Chloro{2-[2,2-dimethyl-1-(methylamino)propyl]phenyl-C,N}{*tert*-butylmethylphenylphosphine-P}palladium(II), (*S<sub>C</sub>R<sub>N</sub>,R<sub>P</sub>*)/(*S<sub>C</sub>R<sub>N</sub>,S<sub>P</sub>*)-**6e**.** The mixture of the enantiopure dimer (*S<sub>C</sub>R<sub>N</sub>*)-**1e** (0.0953 g, 0.15 mmol,  $[\alpha]_D^{20}$  +169.2 (c 1.076, CH<sub>2</sub>Cl<sub>2</sub>)) and 3 mL of 0.2M solution of the racemic phosphine **P\*** in CH<sub>2</sub>Cl<sub>2</sub> (0.6 mmol) was stirred for 0.5 h under argon at r. t. and evaporated to dryness. The chromatographic purification was performed on the two flash columns (Silpearl, *h* 15 cm, *d* 1.8 cm) using the benzene/acetone 25:1 mixture as an eluent and without any attempts to separate isomers. After the slow recrystallization from benzene/pentane 0.042 g (28% yield) of the complex **6e** was obtained as a mixture of (*S<sub>C</sub>R<sub>N</sub>,R<sub>P</sub>*)/(*S<sub>C</sub>R<sub>N</sub>,S<sub>P</sub>*) diastereomers in the ca. 11:1 ratio (<sup>1</sup>H NMR data): m.p. 168-170°C, *R<sub>f</sub>* 0,37 (Silufol UV-254, benzene/acetone 25:1) for both diastereomers.

<sup>31</sup>P NMR (CH<sub>2</sub>Cl<sub>2</sub>, -60°C): δ 35.54, 38.16 ppm (12:1 ratio); <sup>1</sup>H NMR (two sets of signals in 11:1 ratio): major isomer: δ 1.27 (d, <sup>3</sup>J<sub>PH</sub> 14.9 Hz, 9H, PBU<sup>1</sup>), 1.28 (s, 9H, α-Bu<sup>1</sup>), 1.66 (d, <sup>2</sup>J<sub>PH</sub> 8.4 Hz, 3H, PMe); 2.75 (dd, <sup>3</sup>J<sub>HH</sub> 6.2 Hz, J<sub>PH</sub> 2.6 Hz, 3H, NMe), 3.40 (d, J<sub>PH</sub> 6.1 Hz, 1H, α-CH), 3.79 (br.m, 1H, NH); aromatics: δ 6.17 (m, 1H, C<sup>6</sup>H), 6.57 (dt, <sup>3</sup>J<sub>HH</sub> 7.5 Hz, <sup>4</sup>J<sub>HH</sub> 1.5 Hz, 1H, C<sup>5</sup>H), 6.84 (dt, <sup>3</sup>J<sub>HH</sub> 7.5 Hz, <sup>4</sup>J<sub>HH</sub> 1.3 Hz, 1H, C<sup>4</sup>H), 6.96 (dd, <sup>3</sup>J<sub>HH</sub> 7.5 Hz, <sup>4</sup>J<sub>HH</sub> 1.5 Hz, 1H, C<sup>3</sup>H); 7.49 (m, 3H, PPh), 7.97 (m, 2H, PPh); minor isomer: δ 2.80 (dd, <sup>3</sup>J<sub>HH</sub> 6.3 Hz, J<sub>PH</sub> 2.4 Hz, 3H, NMe); aromatics: δ 6.20 (m, 1H, C<sup>6</sup>H), 6.42 (dt, <sup>3</sup>J<sub>HH</sub> 7.8 Hz, 1H, C<sup>5</sup>H), 6.75 (dt, <sup>3</sup>J<sub>HH</sub> 7.3 Hz, 1H, C<sup>4</sup>H), 6.91 (dd, <sup>3</sup>J<sub>HH</sub> 7.3 Hz, 1H, C<sup>3</sup>H); 7.30 (m, 3H, PPh), 7.70 (m, 2H, PPh); the signals of remaining protons are hidden under the more intensive signals of major isomer.

**Chloro{2-(*tert*-butylaminomethyl)phenyl-C,N}{*tert*-butylmethylphenylphosphine-P}-palladium(II), (*S<sub>N</sub>,R<sub>P</sub>*)\*/(*S<sub>N</sub>,S<sub>P</sub>*)\*-**6g**.** The mixture of racemic dimer **1g** (0.2002 g, 0.33 mmol) and 7.8 mL of 0.1M solution of racemic phosphine **P\*** in CH<sub>2</sub>Cl<sub>2</sub> (0.78 mmol) was stirred for 0.5 h at r. t. and evaporated to dryness. After the purification on the several flash columns of SiO<sub>2</sub> (Silpearl, *h* 15 cm, *d* 2.5 cm) using the benzene/acetone 5:1 mixture as an eluent and lowtemperature recrystallization from benzene/pentane the

mixture of diastereomeric racemates ( $S_N, R_P$ )\*/( $S_N, S_P$ )\*-6g was isolated in the yield of 9.3% (0.0297 g): m.p. 151-153°C,  $R_f$  0.57 (Silufol UV-254, benzene/acetone 5:1) for both diastereomers.

$^{31}\text{P}$  NMR ( $\text{CH}_2\text{Cl}_2$ ,  $-60^\circ\text{C}$ ):  $\delta$  36.69, 37.54 ppm (12:1 ratio);  $^1\text{H}$  NMR (r.t., two sets of signals in 5:1 ratio): major isomer:  $\delta$  1.29 (d,  $^3J_{\text{PH}}$  17.6 Hz, 9H,  $\text{PBU}^1$ ), 1.19 (s, 9H,  $\text{NBU}^1$ ), 1.61 (d,  $^2J_{\text{PH}}$  10.4 Hz, 3H,  $\text{PMe}$ ); 3.85 (dd,  $^2J_{\text{HH}}$  14.7 Hz,  $^4J_{\text{PH}}$  5.3 Hz, 1H,  $\alpha\text{-CH}^6$ ), 4.73 (dd,  $^2J_{\text{HH}}$  14.7 Hz,  $^3J_{\text{HH}}$  6.7 Hz, 1H,  $\alpha\text{-CH}^4$ ), 4.1 (br.t, 1H, NH); aromatics:  $\delta$  6.04 (m, 1H,  $\text{C}^6\text{H}$ ), 6.53 (m,  $^3J_{\text{HH}}$  7.2 Hz, 1H,  $\text{C}^5\text{H}$ ), 6.80 (dt, 1H,  $^3J_{\text{HH}}$  6.2 Hz,  $^4J_{\text{HH}}$  1.2 Hz,  $\text{C}^4\text{H}$ ), 6.87 (dd,  $^3J_{\text{HH}}$  7.2 Hz, 1H,  $\text{C}^3\text{H}$ ); 7.48 (m, 3H, PPh), 8.00 (m, 2H, PPh); minor isomer:  $\delta$  1.32 (d,  $^3J_{\text{PH}}$  17.0 Hz, 9H,  $\text{PBU}^1$ ), 1.21 (s, 9H,  $\text{NBU}^1$ ), 3.88 (dd,  $^2J_{\text{HH}}$  14.5 Hz,  $^4J_{\text{PH}}$  5.5 Hz, 1H,  $\alpha\text{-CH}$ ), 4.67 (dd,  $^2J_{\text{HH}}$  14.5 Hz,  $^3J_{\text{HH}}$  6.5 Hz, 1H,  $\alpha\text{-CH}$ ); aromatics:  $\delta$  6.14 (m, 1H,  $\text{C}^6\text{H}$ ), 6.38 (dt,  $^3J_{\text{HH}}$  7.2 Hz, 1H,  $\text{C}^4\text{H}$  or  $\text{C}^5\text{H}$ ), 6.73 (dt,  $^3J_{\text{HH}}$  7.2 Hz, 1H,  $\text{C}^5\text{H}$  or  $\text{C}^4\text{H}$ ), 6.85 (m, 1H,  $\text{C}^3\text{H}$ ); 7.36 (m, 3H, PPh), 7.78 (m, 2H, PPh); the signals of remaining protons are hidden under the more intensive signals of major isomer.

**Chloro{2-[1'-methylpyrrolidin-2'-yl]phenyl-C,N}{*tert*-butylmethylphenylphosphine-P}-palladium(II), ( $R_C R_N R_P$ )-8 and ( $R_C R_N S_P$ )-8.** The mixture of the enantiopure dimer ( $R_C R_N$ )-4 (0.0906 g, 0.15 mmol,  $[\alpha]_{\text{D}}^{20} -227$  (c 0.32,  $\text{CHCl}_3$ )) and 3 mL of 0.2M solution of the racemic phosphine P\* in  $\text{CH}_2\text{Cl}_2$  (0.6 mmol) was stirred under argon for 0.5 h at r. t. and evaporated to dryness. The chromatographic separation of two diastereomers was performed on the several flash columns (Silicagel,  $h$  20 cm,  $d$  1.8 cm) using the ether/pentane 1:1 mixture as an eluent. After the recrystallization from ether/pentane the major ( $R_C R_N R_P$ )-isomer of monophosphine adduct 8 was obtained as the light-yellow crystals in an optical pure state in the yield of 30% (0.0434 g): m.p. 70-72°C,  $R_f$  0.51 (Silufol UV-254, ether/pentane 1:1). Anal. Calc.: C, 56.12; H, 7.43; N, 2.52 for  $\text{C}_{22}\text{H}_{31}\text{ClNPPdEt}_2\text{O}$ . Found: C, 56.14; H, 7.22; N, 2.55.

$^{31}\text{P}$  NMR ( $\text{CH}_2\text{Cl}_2$ , r. t.):  $\delta$  37.33 ppm;  $^1\text{H}$  NMR:  $\delta$  1.30 (d,  $^3J_{\text{PH}}$  14.9 Hz, 9H,  $\text{PBU}^1$ ), 1.64 (d,  $^2J_{\text{PH}}$  9.1 Hz, 3H,  $\text{PMe}$ ); 2.60 (d,  $^4J_{\text{PH}}$  2.0 Hz, 3H,  $\text{NMe}$ ); aromatics:  $\delta$  6.30 (m, 1H,  $\text{C}^6\text{H}$ ), 6.58 (dt,  $^3J_{\text{HH}}$  7.5 Hz,  $^4J_{\text{HH}}$  1.5 Hz, 1H,  $\text{C}^5\text{H}$ ), 6.85 (dt,  $^3J_{\text{HH}}$  7.5 Hz,  $^4J_{\text{HH}}$  1.3 Hz, 1H,  $\text{C}^4\text{H}$ ), 6.97 (dd,  $^3J_{\text{HH}}$  7.5 Hz,  $^4J_{\text{HH}}$  1.5 Hz, 1H,  $\text{C}^3\text{H}$ ); 7.5 (m, 3H, PPh), 7.98 (m, 2H, PPh); pyrrolidine ring protons:  $\delta$  1.95 (m, 1H), 2.17 (m, 1H), 2.35 (m, 1H), 2.46 (m, 1H), 2.58 (m, 1H), 3.48 (m, 1H), 4.55 (m, 1H,  $\text{C}^2\text{H}$ ); solvate  $\text{Et}_2\text{O}$ :  $\delta$  1.21 (t,  $^3J_{\text{HH}}$  6.9 Hz, 6H,  $\text{CH}_3$ ), 3.48 (q,  $^3J_{\text{HH}}$  6.9 Hz, 4H,  $\text{CH}_2$ ).

The minor isomer ( $R_C R_N S_P$ )-8 was isolated as a light-yellow viscous oil; it contains 10% of ( $R_C R_N R_P$ )-diastereomer admixture (80% *de*,  $^1\text{H}$  NMR data):  $R_f$  0.43 (Silufol UV-254, ether/pentane 1:1).

$^{31}\text{P}$  NMR ( $\text{CH}_2\text{Cl}_2$ , r. t.):  $\delta$  36.75 ppm;  $^1\text{H}$  NMR:  $\delta$  1.30 (d,  $^3J_{\text{PH}}$  14.4 Hz, 9H,  $\text{PBU}^1$ ), 1.72 (d,  $^2J_{\text{PH}}$  9.3 Hz, 3H,  $\text{PMe}$ ); 2.64 (d,  $^4J_{\text{PH}}$  2.0 Hz, 3H,  $\text{NMe}$ ); aromatics:  $\delta$  6.15 (m, 1H,  $\text{C}^6\text{H}$ ), 6.35 (d.t.,  $^3J_{\text{HH}}$  7.7 Hz,  $^4J_{\text{HH}}$  1.5 Hz, 1H,  $\text{C}^5\text{H}$ ), 6.53 (dt,  $^3J_{\text{HH}}$  7.3 Hz,  $^4J_{\text{HH}}$  1.2 Hz, 1H,  $\text{C}^4\text{H}$ ), 6.90 (d.d.,  $^3J_{\text{HH}}$  7.7 Hz,  $^4J_{\text{HH}}$  1.5 Hz, 1H,  $\text{C}^3\text{H}$ ); 7.26 (m, 2H, PPh), 7.32 (m, 1H, PPh), 7.60 (m, 2H, PPh); pyrrolidine ring protons:  $\delta$  1.95 (m, 1H), 2.20 (m, 1H), 2.36 (m, 1H), 2.48 (m, 1H), 2.62 (m, 1H), 3.50 (m, 1H), 4.54 (m, 1H,  $\text{C}^2\text{H}$ ).

### The study of D/P\* complexation in solution.

All the reactions were performed on vacuum line in the glass tube fused with a top-side-arranged NMR ampoule.

The calculated amount of dimer 1, 2 or 4 was placed into the tube containing glassbreaker and racemic phosphine P\*, enclosed into the thin-walled glass phial. After the tube was attached to vacuum line and evacuated ( $10^{-2}$  torr) the fixed amount of oxygen-free  $d_2$ -methylene chloride was vacuum-transferred into the tube which was then sealed off. The phosphine containing phial was broken, the reaction mixture was stirred at room temperature for 30 min and transferred with caution into the NMR ampoule. After the washing of the stem (by stroking them with cotton wool soaked in liquid nitrogen) the ampoule was sealed off and used for the  $^{31}\text{P}$  NMR measurement at  $188 \pm 5$  K.

Evaluation of equilibrium constant  $K$  values was made on the base of integral intensities ( $I_M$ ) of  $^{31}\text{P}$  NMR signals from two diastereomeric monophosphine adducts  $M$  (6-8) according to the equation 8 in the case of racemic complexes  $D^*$  ( $P^*/Pd$  ratio ca. 1.1:1).

$$K = \frac{I_{(SR,R)^*-M}}{I_{(SR,S)^*-M}} \quad (8)$$

Here and later on we shall consider the formation of predominant diastereomer from minor one ( $K > 1$ ) for the convenience of discussion.

For the systems involving the homochiral complexes  $D$  ( $P^*/Pd$  ratio ca. 2) the calculations were performed using the integral intensities of monophosphine diastereomers  $M$  and that of uncomplexed phosphine  $P^*$  without regard for bisphosphine complexes according to the equation 9 derived from eq. 4.

$$K = \frac{I_{(SR,R)^*-M}\{I_P + \Delta I_M\}}{I_{(SR,S)^*-M}\{I_P - \Delta I_M\}} \quad (9)$$

where  $I_P$  designates the integral intensity of the uncomplexed phosphine signal and the term  $\Delta I_M = I_{(SR,R)-M} - I_{(SR,S)-M}$  denotes the difference in integral intensities between the signals of major and minor diastereomers of monophosphine complex  $M$ , respectively.

The limits of constant  $K$  variation depending on the stereochemical composition of bisphosphine species were estimated using the most general form of equation for the equilibrium constant (eq. 10):

$$K = \frac{I_{(SR,R)^*-M}\{I_P + \Delta I_M + \Delta I_B\}}{I_{(SR,S)^*-M}\{I_P - \Delta I_M - \Delta I_B\}} \quad (10)$$

where  $\Delta I_B = I_{(SR,R,R)-B} - I_{(SR,S,S)-B}$  and substituting the integral intensity of the most intensive signal in the range of  $B$  resonance for the first or second term and zero for the another term.

As the measure of palladacycle dechelation we have chosen here the relative content of bisphosphine species among all  $Pd(II)$  containing species in the reaction mixture (eq. 9):

$$\frac{[B_i]}{[M_i] + [B_i]} = \frac{0.5 I_B}{I_M + 0.5 I_B} \quad (11)$$

where  $[B_i]$ ,  $I_B$  and  $[M_i]$ ,  $I_M$  denote the total concentration and integral intensity of signals of all isomeric bisphosphine species and that of two diastereomers of monophosphine adduct, respectively.

The  $P^*/Pd$  ratio was calculated according to the equation 12 using the integral intensities of corresponding signals:

$$P^*/Pd = \frac{[P] + [M] + 2 [B_i]}{[M_i] + [B_i]} = \frac{I_P + I_M + I_B}{I_M + 0.5 I_B} \quad (12)$$

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