Asymmetric exchange of cyclopalladated ligands: a new route to optically active phosphapalladacycles

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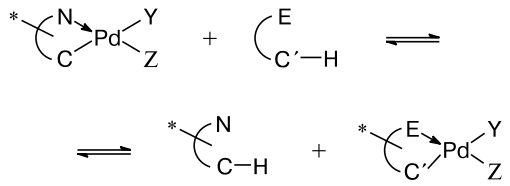
An asymmetric version of the cyclopalladated ligand exchange reaction was developed. This procedure involves the use of prochiral phosphines in an aprotic medium. A benzylaminate palladacycle bearing the primary amino group and the bulky Bu^t substituent at the *C** stereocenter serves as a chirality inductor.

Key words: asymmetric induction, C—H bond activation, cyclopalladated ligand exchange, optically active phospha- and azapalladacycles, X-ray diffraction analysis.

Although the idea of asymmetric C—H bond activation by transition metals is attractive, examples of this process are scarce. In a special case of cyclopalladation, two versions of asymmetric C—H bond activation under control of either external sources of chirality (bases)[1—7] or inner-sphere sources are known. Bidentate *N*,*N*- [8,9] and *P*,*P*-donor[10,11] ligands were tested as the latter sources. The chirality transfer from chelated ligands proved to be highly efficient in the closure of *C***O*-[9] and *C***C*-palladacycles* (see Refs 8, 10, and 11), whereas an attempt to generate planar chirality upon the formation of a *CN*-palladacycle with the use of an optically active monodentate *S**-donor ligand (sulfoxide) in a metallating agent failed.[12] Chelation of phosphino-*P*-ylides giving rise to *PC**-palladacycles with diastereoselectivity of ~70% *de* (see Refs 13 and 14) is the only example of the use of *CN*-palladacycles as chirality inductors. However, configurational lability of such systems substantially limits their use.

The aim of the present study was to develop a new method of asymmetric C—H bond activation based on cyclopalladated ligand exchange (CLE**)[15,16] (Scheme 1).

Scheme 1



Although the starting palladacycle in the CLE reaction can serve not only as the metallating agent but also as the source of chirality, only achiral versions of this reaction have been examined. The only attempt to perform asymmetric CLE has been unsuccessful.[17] High efficiency of cyclopalladated complexes in optical resolution[18,19] and enantioselective catalysis,[20—23] as reagents for the enantiomeric purity determination,[24,25] and as matrices for asymmetric synthesis[26—28] was documented. This stimulated the estimation of their potential as chirality inductors in CLE reactions. The preliminary results of our investigations in this field have been published recently.[29]

Results and Discussion

We chose a series of benzylaminate *CN*-dimers (**1a,b** and **2a—7a**),* which differ in the nature of the amino

* The asymmetric atom directly bound to the metal atom is marked with an asterisk.

** The more laconic term transcyclometallation has been proposed[16] for the description of such reactions; however, this term does not reflects the essence of the process, in which ligands rather than metal atoms (transmetallation) are exchanged.

* The number of the complex corresponds to the superscript n in the code of the starting ligand HL^n, and the letters stand for different derivatives of this palladacycle.

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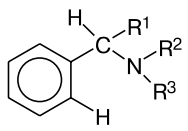
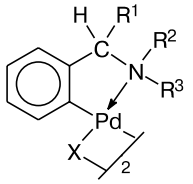
group, the α-substituent, or μ-halide, as chirality inductors.



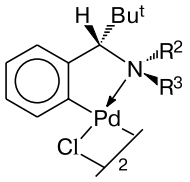
HL[1]—HL[8]



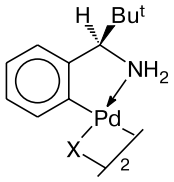
1a,b, 2a—8a

Complex	HL^n	R^1	R^2	R^3
1	**HL[1]**	Bu[t]	H	H
2	**HL[2]**	Bu[t]	H	Me
3	**HL[3]**	Bu[t]	Me	Me
4	**HL[4]**	Ph	H	H
5	**HL[5]**	Me	H	H
6	**HL[6]**	Me	Pr[i]	H
7	**HL[7]**	Me	Me	Me
8	**HL[8]**	Ph	Me	Me

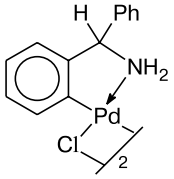
X = Cl (**a**), Br (**1b**)



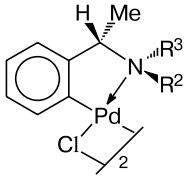
(S_C)-**1a—3a**



(R_C)-**1a,b**

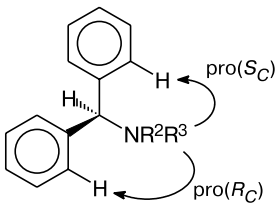


rac-**4a**

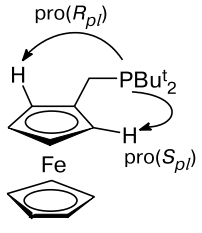


(S_C)-**5a,7a**, (S_CR_N)-**6a**

The *N*- (**HL[1]**, **HL[3]**, **HL[4]**, and **HL[8]**), *P*- (**HL[9]** and **HL[10]**), and *S*-donor ligands (**HL[11]**) (most of which are prochiral) were tested as substrates. This set was intended for estimation of the efficiency of generation of *C**- and *P**-central chirality and planar chirality upon C—H bond activation.*

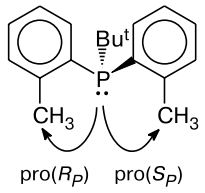


HL[4], **HL[8]**

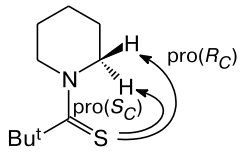


HL[9]

* New dimeric cyclopalladated complexes **1b**, **4a**, and **11a** were characterized as their mononuclear derivatives $[Pd(\eta^2\text{-}L^n)(Q)X]$ (Q = PPh_3, X = Cl (**4b**), Br (**1c**); Q = Py, X = Cl (**11b**)).



HL[10]



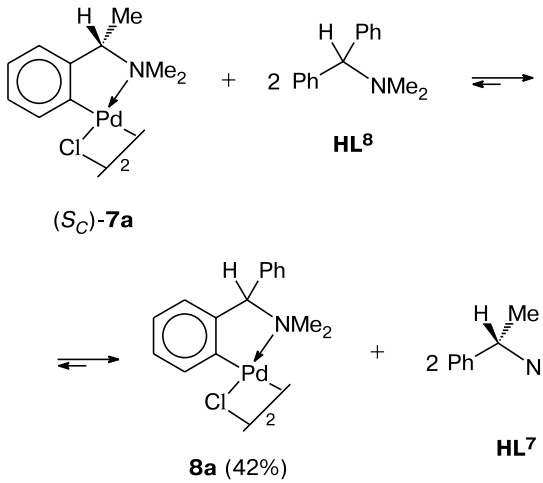
HL[11]

To achieve the goal to be sought, it was necessary to optimize the reaction conditions and the structure of the reagent and to estimate the scope of this reaction.

Optimization of medium

The CLE reactions have as yet been carried out only in an acidic medium, which is necessary for destruction of the starting palladacycle through Pd—C bond protolysis.[15,30] Since monodentate ligands are generally poorly efficient in the chirality transfer, the main goal of the present study was to create conditions for retention of the chelate structure of palladating agents. As expected, the reactions in an acidic medium produced new palladacycles as racemates. For example, the reaction of dimer (S_C)-**7a** with tertiary amine **HL[8]** in an acidic medium afforded racemic dimer **8a** (Scheme 2).

Scheme 2



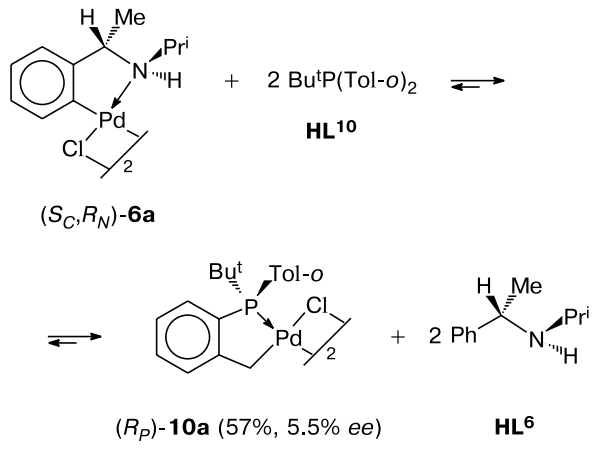
Conditions: PhMe—AcOH, 50 °C, 17 h.

The same results were obtained in the reactions with other *N*-, *P*-, and *S*-donor substrates in an acidic medium. For example, the (S_C)-**1a**/**HL[8]**, (S_C)-**1a**/**HL[10]**, (S_C)-**1a**/**HL[11]**, and (S_CR_N)-**6a**/**HL[10]** systems gave new cyclopalladated complexes **8a**, **10a**, and **11a** as racemates (*ee* <2%) in moderate yields (42—71%). In spite of the absence of asymmetric induction under these conditions, these results are of interest on their own. First, they pro-

vide stereochemical evidence for the dissociative mechanism of the CLE reaction in acidic media.[31,32] Second, these results illustrate the possibility of efficient cyclopalladation of *P*- and *S*-donor substrates in CLE reactions. Only one example of this type of reactions involving a phosphine substrate ($PhCH_2PPh_2$) was documented.[33] This reaction produced a *PC*-palladacycle in low yield (21%). Earlier, thioamides were not used in CLE reactions. Of *S*-containing substrates, only thioketone, thiourea, and bis(thioether) were tested in this reaction.[34]

We performed the CLE reaction in an *aprotic medium* for the first time with the use of the (S_CR_N)-**6a**/**HL**[10] system. This reaction in toluene under heating (in the absence of acids) gave new dimer **10a** in a yield identical to that obtained in an acidic medium (Scheme 3).

Scheme 3



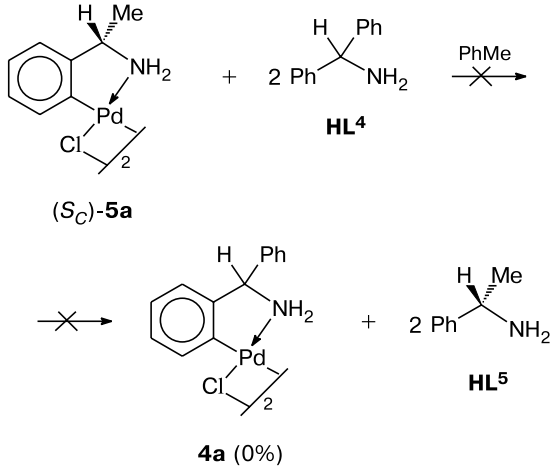
Conditions: PhMe, 60 °C, 11 h.

The CLE reaction should be performed in an aprotic medium, which is the key prerequisite to the development of its asymmetric version. However, to increase the degree of stereodifferentiation, it is necessary to optimize the structures of the palladating agent and the substrate, as well as the reaction conditions.

Nature of substrates

The nature of the substrate has a substantial influence on the efficiency of C—H bond activation in an aprotic medium. In the absence of acids, the reactions of dimers (S_C)-**1a** and (S_C)-**5a** with tertiary amines **HL**[3] and primary amines (**HL**[4]) stopped at the formation of the mononuclear adducts [Pd(η^2-L^n)(**HL**´)Cl] (**HL**´ = **HL**[3] (**5b**) or **HL**[4] (**1d**, **5c**)). Neither dehalogenation of the reagent (KPF_6, MeCN) nor heating led to activation of the (S_C)-**5a**/**HL**[3] system. In the (S_C)-**5a**/**HL**[4] system, the formation of dimer **4a** was not observed both at room temperature and upon heating (Scheme 4).

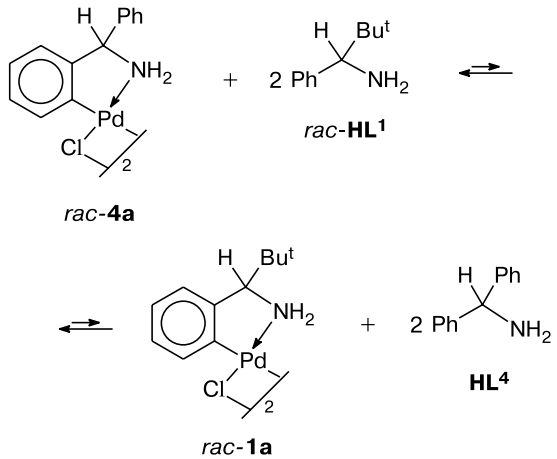
Scheme 4



Conditions: 20 °C, 168 h or 50 °C, 192 h.

The reaction of dimer **4a** with primary amine **HL**[1] bearing the bulky But substituent at the α position (the reaction was performed with racemates) is the only exception. After an extremely long period of storage (2.5 months) of this reaction mixture at room temperature, the formation of new *CN*-palladacycle **1a** with a low degree of conversion (18%) was spectroscopically established (Scheme 5).

Scheme 5



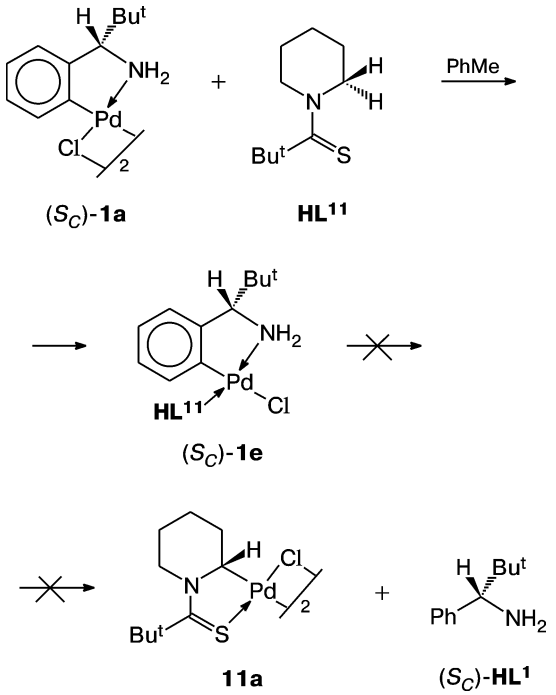
Conditions: toluene, 20 °C, 2.5 months.

The results of investigation of the reactions of *CN*-palladacycles with amines suggested that the depth of CLE in an aprotic medium is determined by the relative

ease of cyclopalladation of two benzylamines and the strength of coordination of the incoming ligand to the reagent. Actually, the primary amino group of the ligand **HL[1]** ensures its stronger coordination to Pd^{II} compared to the tertiary analog **HL[3]**, whereas the bulky α-Bu^t substituent more efficiently sterically promotes[35] its cyclopalladation compared to the α-Me- (**HL[5]**) or α-Ph group (**HL[4]**) in other primary benzylamines. Although the CLE reaction in an aprotic medium proved to be possible even with the involvement of the ligand containing the hard *N*-donor atom, the development of the chiral version holds little promise because of long reaction times.

We expected that the reactions of palladacycles with *N*-thiopivaloylpiperidine (**HL[11]**) could be promoted by both the soft sulfur atom of the substrate, which can form a strong coordination bond with palladium(II), and the bulky Bu^t group of the acyl fragment, which is sterically favorable for cyclopalladation.[35,36] However, all attempts to perform CLE in the (S_C)-**1a**/**HL[11]** system in an aprotic medium failed. Neither heating nor dehalogenation of the reactant promoted this reaction, and it stopped (TLC data) at the formation of the adduct of the *CN*-palladacycle with thioamide (**1e**) (Scheme 6).

Scheme 6



Conditions: 20 °C, 21 days or 60 °C, 10 days, or KPF_6, MeCN, 20 °C, 28 h.

This failure is evidence that the efficiency of C—H bond activation in the substrate in an aprotic medium depends substantially on the relative ability of two ligands to undergo cyclopalladation. Actually, of the two ligands, **HL[1]** and **HL[11]**, which function in the (S_C)-**1a**/**HL[11]** system, the former ligand may be subjected to cyclopalladation even at room temperature,[37] whereas the latter ligand is involved in the reaction only on heating. The problem of strong binding of the substrate to the reagent is more radically solved with the use of phosphine ligands bearing the soft *P*-donor atom. Because of this, a further study of the factors responsible for the efficiency of CLE was carried out with the use of prochiral phosphines P(Tol-*o*)$_2$$Bu^t$ and $FcCH_2PBu^t_2$.

Optimization of the structure of cyclopalladated reagents

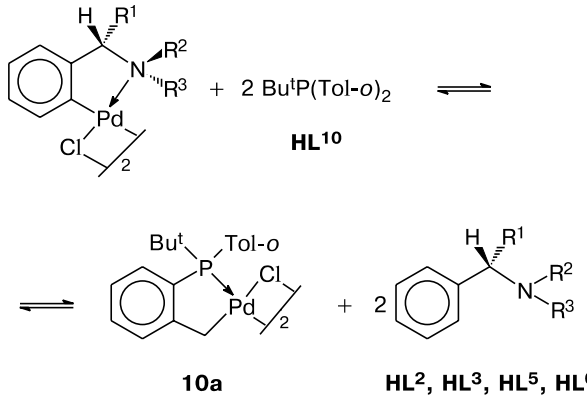
For the development of the asymmetric version of CLE, it is necessary to have a highly efficient palladating agent, which enables this process to be performed under mild temperature conditions. Most of the known reactions of this type were performed in an acidic medium with heating (50—118 °C).[30,32,34,38,39] The below-described experiments revealed the structural factors responsible for the efficiency of *CN*-reagents in CLE reactions performed in an aprotic medium.

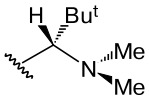
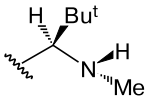
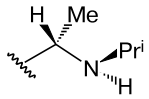
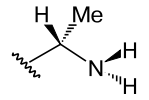
A comparison of the reactions of phosphine **HL[10]** with *CN*-dimers clearly shows that the position of the equilibrium between two palladacycles depends on the ease of C—H bond activation in the corresponding benzylamine (Scheme 7).

Actually, heating of phosphine **HL[10]** with α-Bu^t-substituted reagents (S_C)-**3** and (R_CS_N)-**2a** led to the formation of *PC*-complex **10a** in low yield (8%) only in the latter system (with the reagent containing the secondary amino group). A comparison of the reactions of phosphine **HL[10]** with α-Me-substituted dimers (S_CR_N)-**6a** and (S_C)-**5a** illustrates the same tendency. The reaction of reagent **5a** containing the primary amino group produces *PC*-dimer **10a** in 66% yield, which is the maximum value for the reactions in aprotic media at room temperature, whereas the reaction with secondary amine derivative **6a** requires heating. The influence of the size of the α-substituent in the palladacycle of the reagent is evident from a comparison of the reactions of **HL[10]** with two secondary amine derivatives. Thus, α-Me-substituted dimer (S_CR_N)-**6a** provides a seven times higher yield during the period of time, which is an order of magnitude shorter than that required in the case of α-Bu^t-substituted analog (R_CS_N)-**2a**.

The influence of the structure of the reagent is even more pronounced in the reactions of ferrocenylmethylphosphine **HL[9]** (Scheme 8) due to its lower ability to undergo cyclopalladation[40] compared to diarylphosphine **HL[10]** (see Ref. 41). Actually, the reaction of **HL[9]** with α-Bu^t-substituted reagents at 20 °C (500 h) stopped at the formation of the mononuclear adduct

Scheme 7



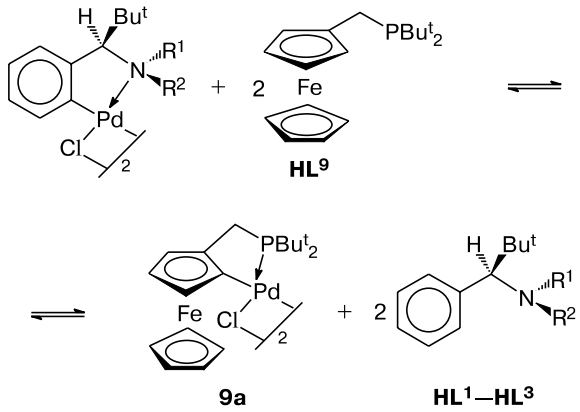
Reagent	Structural fragment	Conditions		Yield **10a** (%)	*ee* (%)
		T/°C (toluene)	τ/h		
(S_C)-**3a**		20	792	—	
		60	240	Traces	
(R_CS_N)-**2a**		60	132	8	8.8 (S_P)
(S_CR_N)-**6a**		60	11	57	5.5 (R_P)
(S_C)-**5a**		20	336	66	13.4 (R_P)

$[Pd(\eta^2\text{-}L')(\mathbf{HL^9})Cl]$ (**HL′** = **HL¹** (**1f**), **HL²** (**2b**), or **HL³** (**3b**)). Trace amounts of *PC*-dimer **9a** (TLC data) were detected only in the reactions with the primary benzylamine derivative (**1a**). The higher reactivity of reagent **1a** is evident from a comparison of the CLE reactions at high temperature. Dimers **2a** and **3a** derived from secondary and ternary amines, respectively, virtually do not react with phosphine **HL⁹** even at 60 °C, whereas the reaction with reagent (R_C)-**1a** produces *PC*-complex (S_{pl})-**9a** in 26% yield, but the enantiomeric excess is only moderate (*ee* 44%).

The data presented in Schemes 7 and 8 indicate that there is an inverse dependence of the shift of the equilibrium between *CN*- and *PC*-palladacycles toward the latter on the ability of the starting benzylamines to undergo *ortho*-palladation. A comparison of the conditions and results of cyclopalladation (Li_2PdCl_4/AcONa, MeOH) of a series of benzylamines, which differ in the structure of the side chain, confirms this conclusion (Table 1).

$$\mathbf{HL^3} > \mathbf{HL^2} \approx \mathbf{HL^6} \approx \mathbf{HL^1} \gg \mathbf{HL^5}$$

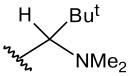
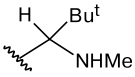
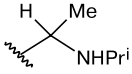
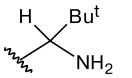
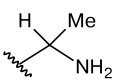
Scheme 8



Reagent	Fragment NR^1R^2	Conditions		Yield **9a** (%)
		T/°C (toluene)	τ/h	
(S_C)-**3a**	NMe_2, *ent*	60	420	Traces
(S_CR_N)-**2a**	NHMe	60	420	Traces
(R_C)-**1a**	NH_2	20	316	Traces
	NH_2	60	48	26 (*ee* 44% (S_{pl}))

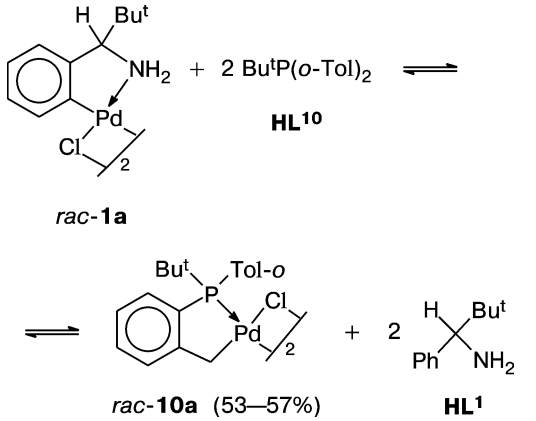
Actually, *ortho*-palladation of ternary amine **HL³** can proceed in high yield even at 0 °C. This reaction with secondary amines requires a longer reaction time (**HL²**) and/or an rise of the temperature (**HL²** or **HL⁶**). The relatively high reactivity of primary α-But-substituted benzylamine **HL¹** results from steric promotion of the reaction. It is known[35] that sterically unhindered primary benzylamines (for example, **HL⁵**) do not form palladacycles under such mild conditions.

Table 1. Cyclopalladation of benzylamines

HL^n		Condition		Yield	Reference
		T/°C	τ/h		
	**HL³**	0—2	~8	78—83	37
	**HL²**	20	40	60	42
	**HL⁶**	65	3	84	43
	**HL¹**	20	23	50	44
	**HL⁵**	20	Δ	0	35, 45, 46

The presence of a free coordination site in a metallating agent often increases its efficiency.[47,48] However, an attempt to increase the reactivity of reagent **1a** in CLE by its dehalogenation did not meet with success. The reactions of **HL**[10] with the solvated palladacycles $[Pd(\eta^2\text{-}\mathbf{L^1})(Solv)_2]^+$ in MeCN or acetone produced *PC*-dimer **10a** in an only slightly higher yield compared to that achieved in the reaction with μ-chloride dimer **1a** at the same temperature (57% or 53% and 48%, respectively), the reaction time being substantially longer (Scheme 9). Hence, analogous experiments with enantiomerically pure reagent (R_C)-**1a** were not performed.

Scheme 9



Reagents and conditions: KPF_6, MeCN or Me_2CO, 20 °C, 45 days.

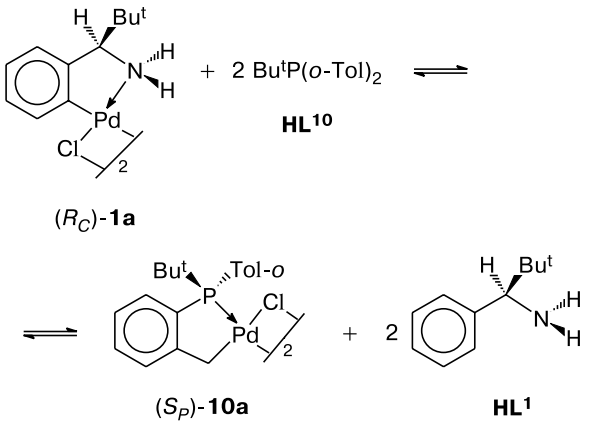
Enantioselectivity of cyclopalladated ligand exchange

Although we succeeded in performing CLE with particular substrates in an aprotic medium, the stereochemical characteristics of this process remained unsatisfactory (*ee* < 44%). To optimize the structure of reagents for asymmetric CLE, it was necessary to find a compromise between the opposite requirements imposed on the *CN*-palladacycle as the metallating agent and the chirality inductor. It is known that palladacycles based on bulky ligands have a pronounced chiral recognition ability, but these ligands are less reactive in CLE compared to cyclopalladated complexes based on sterically unhindered benzylamines (see above). It was reasonable to expect that enantiomers of the palladacycle based on primary α-Bu^t-substituted benzylamine, *viz.*, (R_C)-**1a** and (S_C)-**1a**, might be the reagent of choice for asymmetric CLE, because the primary amino group in the starting ligands decreases its ability to undergo cyclometallation, which is favorable for a shift of the equilibrium between the *CN*- and *PC*-complexes toward the latter, whereas the bulky α-Bu^t group ensures conformational stability of the *CN*-palladacycle,[44] thus increasing its ability for chiral discrimination.[49]

However, even this reagent ensures only moderate induction of planar chirality. Thus, the reaction of dimer (R_C)-**1a** with ferrocenylmethylphosphine **HL**[9] produced *PC*-complex (S_{pl})-**9a** with *ee* 44% (see Scheme 8). A relatively low degree of asymmetric induction in this reaction is partially attributed to the fact that the reaction was performed at high temperature (60 °C) because of a low ability of trialkylphosphine **HL**[9] to undergo cyclopalladation.[40]

Reagent (R_C)-**1a** proved to be more efficient as the inductor of the *P**-central chirality. The reaction of this compound with phosphine **HL**[10] even at high temperature (60 °C) produced dimer (S_P)-**10a** in satisfactory optical yield (*ee* 66%) (Scheme 10). A further increase in asymmetric induction in the (R_C)-**1a**/**HL**[10] system was achieved by decreasing the temperature. The optical yield of *PC*-dimer (S_P)-**10a** increases to *ee* 72% at 20 °C and then to *ee* 86% at −13 °C, although at the expense of an increase in the reaction time (from 2.5 to 165 days).

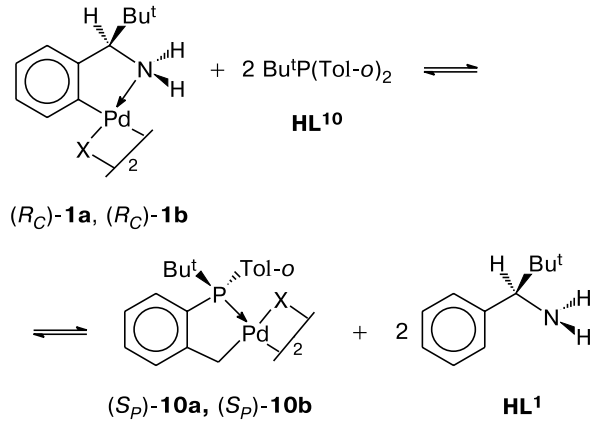
Scheme 10



Conditions		Yield (S_P)-**10a** (%)	*ee* (%)
T/°C	τ/h (toluene)		
60	58	24	66
20	140	48	72
−13	5.5 months	13	86.4

Then we estimated the effect of the nature of the anion in the palladating agent on the rate and enantioselectivity of CLE. It was expected that the replacement of the chloride anion by the bulkier anion would increase the steric demands of the reagent. For this purpose, we studied the reactions of μ-chloride dimer (R_C)-**1a** and its μ-bromide analog (R_C)-**1b** with phosphine **HL**[10] under identical conditions (Scheme 11).

Scheme 11



X = Cl (**a**), Br (**b**)

Compound	Conditions		Yield (%)	*ee* (%)
	T/°C (toluene)	τ/h		
(S_P)-**10a**	20	528	30	81
(S_P)-**10b**	20	528	54	91

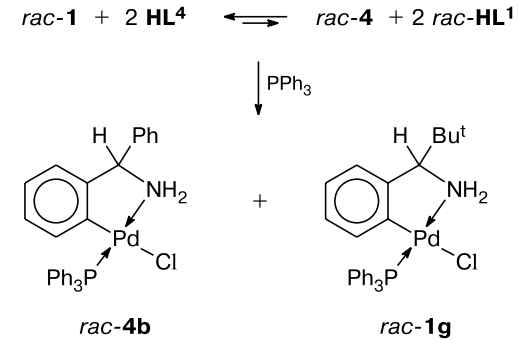
The results of the study confirmed the advantages of μ-bromide reagent (R_C)-**1b** concerning both the reactivity and enantioselectivity. First, the enantiomeric purity of *PC*-palladacycle (S_P)-**10b** (*ee* 91%) isolated in the reaction with (R_C)-**1b** is higher than that observed in experiments with μ-chloride analog (R_C)-**1a** at the same temperature (*ee* 81%) or even at negative temperature (*ee* 86%). Second, the substantially higher reactivity of reagent **1b** is evident from the almost twofold increase in the yield of the *PC*-dimer and an increase in the reaction rate. The ^{31}P NMR monitoring of the reactions of phosphine **HL^{10}** with dimers (R_C)-**1b** and (R_C)-**1a** showed that after 54 h the total percentage of different forms of the *PC*-palladacycle was 86 and 36%, respectively. The observed increase in the rate and enantioselectivity of CLE in going from μ-Cl to μ-Br is the first example of an increase in the efficiency of palladacycles in the chiral recognition with the use of such a simple modification of its coordination environment.

Experimental technique

The choice of the method for monitoring the course of the reaction and its selectivity (TLC, ^{1}H and/or ^{31}P NMR, polarimetry) was governed by the structures of CLE participants. To estimate the degree of conversion, mixtures of different forms of two palladacycles were transformed into dimeric cyclopalladated complexes, which were additionally purified by chromatography. The intermediate mononuclear adducts were identified based on the spectroscopic and TLC parameters of the corresponding authentic complexes isolated or generated *in situ*.

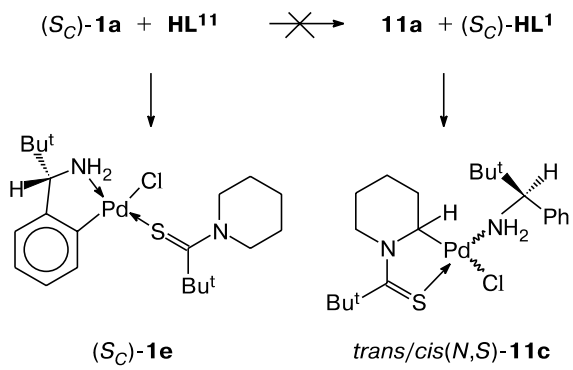
In the reactions with *N*-donor substrates, the transformations of mononuclear species into the corresponding dimers were achieved by protonation of Pd-coordinated benzylamine. The course of the CLE reactions in these systems was qualitatively monitored by TLC in the case of a rather large difference in the chromatographic mobility of the starting and target dimers (ΔR_f 0.26—0.42). The TLC and ^{1}H NMR methods appeared to be inapplicable only to the *rac*-**1a**/**HL^4** and *rac*-**4a**/*rac*-**HL^1** systems because of similar chromatographic mobilities of dimers **1a** and **4a** (ΔR_f ~0.05) and the presence of a large number of isomers (*cis*/*trans* and *meso*/*rac* forms of dimeric cyclopalladated complexes and diastereomers of mononuclear adducts of **4a** with racemic amine **HL^1**). These obstacles were overcome by the *in situ* transformation of a mixture of dimers *rac*-**4a**/*rac*-**1a** into a mixture of two mononuclear derivatives with achiral phosphine PPh_3 *rac*-**4b**/*rac*-**1g**, whose ratio (4.6 : 1) was evaluated by ^{31}P NMR spectroscopy (Scheme 12).

Scheme 12

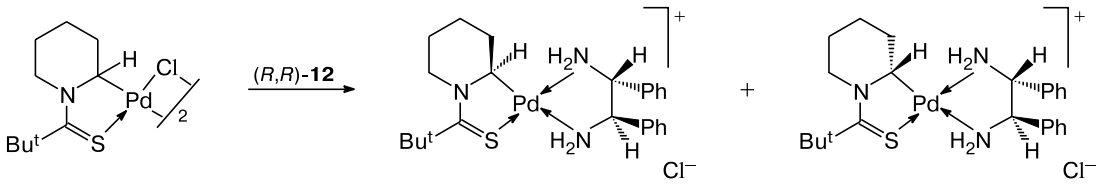


The enantiomeric composition of *CN*-palladacycle **8a**, which was formed in the reactions of *CN*-dimers (S_C)-**1a** and (S_C)-**5a** with amine **HL^8** in an acidic medium, was determined by ^{1}H NMR spectroscopy after *in situ* chiral

Scheme 13



Scheme 14



(*R*,*S*)-**11a** (*R*,*RR*)-**11d** (*S*,*RR*)-**11d**

Conditions: MeOH, 20 °C, 4 h.

derivatization of dimer **8a** with (*S*)-prolinate ((*S*)-Prol). The signals of diastereomers of the adduct [(η^2-L^8)Pd{(*S*)-Prol}] (**8b**)[50] are well resolved, which confirms the validity of the conclusion about the absence of asymmetric induction under these conditions.

Both *CS*-dimer **11a** and the adduct of *CN*-reagent **1a** with thioamide (**1e**) were found to be produced in the reaction of the complex of (S_C)-**1a** with thioamide **HL**[11], which was monitored by chromatography and ^{1}H NMR spectroscopy (Scheme 13).

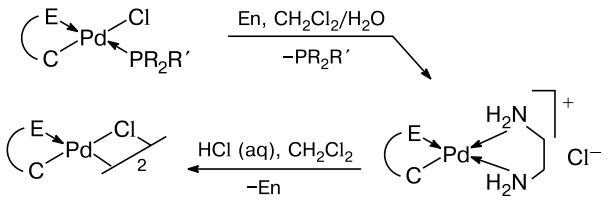
The fact that the reaction in an aprotic medium stops at the formation of adduct **1e** was confirmed by ^{1}H NMR spectroscopy. The absence of the expected adduct of the *CS*-palladacycle with primary amine (**11c**) in the reaction mixture was also confirmed by ^{1}H NMR spectroscopy and the *in situ* generation of this adduct by the reaction of dimer *rac*-**11a** with amine **HL**[1]. It should be noted that the comparable *trans* effects of the *C*- and *S*-donor atoms of the *CS*-palladacycle leads to the formation of adduct **11c** as a 3 : 1 mixture of *trans*(*N*,*S*)/*cis*(*N*,*S*) isomers.

Since coordination of *CS*-palladacycle **11a** with monodentate and unsymmetrical bidentate ligands is characterized by low regioselectivity, chiral derivatization of this compound was performed with the use of the C_2-symmetric auxiliary ligand (1*R*,2*R*)-1,2-diphenylethane-1,2-diamine ((*R*,*R*)-**12**). The formation of *CS*-dimer **11a** as a racemate in an acidic medium was confirmed by ^{1}H NMR spectroscopy based on the ratio of signals corresponding to diastereomers (1 : 1) of cationic derivative **11d** (Scheme 14).

In the CLE reactions with phosphines, the conversion of their highly stable adducts with *CN*-palladacycles into the corresponding dimers required the use of the known[51] method of decoordination of phosphine with an excess of an easily accessible chelating agent, *viz.*, ethylenediamine (En), followed by protolytic removal of the auxiliary ligand En from the intermediate cationic complex (Scheme 15).

Stereoselectivity of CLE with phosphines was estimated by ^{31}P NMR spectroscopy after *in situ* chiral derivatization of dimers **9a** and **10a,b** with (*S*)-prolinate giving rise to adducts **9b** and **10c**, respectively. In spite

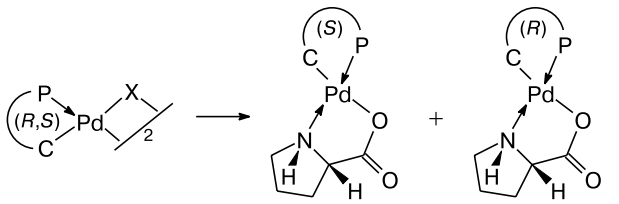
Scheme 15



E = N or P

of the formation of complex **10c** as mixtures of *cis*/*trans* isomers,[41] the spectral pattern remains rather simple for the exact integration (Scheme 16).

Scheme 16



(*R*,*S*)-**9a** (S,S_CS_N)-**9b** (R,S_CS_N)-**9b**
(*R*,*S*)-**10a,b** (S,S_CS_N)-**10c** (R,S_CS_N)-**10c**

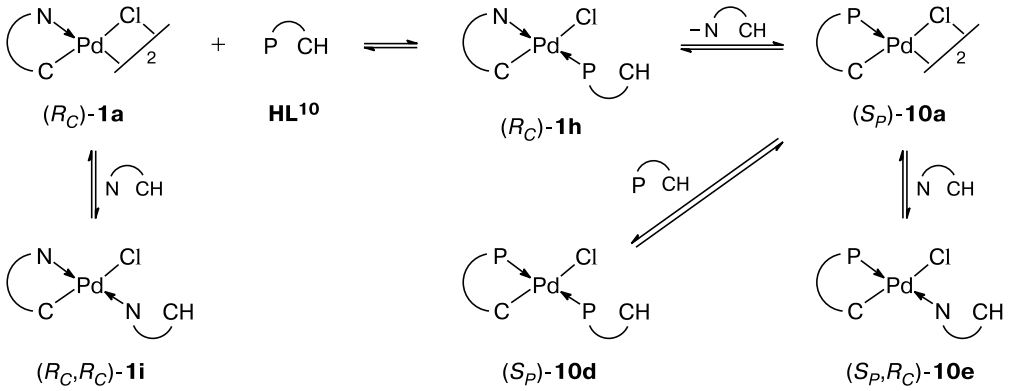
P⌒CH = **HL**[9], **HL**[10]; X = Cl (**9a, 10a**), Br (**10b**)

Reagents and conditions: 1) (*S*)-ProlK, MeOH; 2) $CDCl_3$, ^{31}P NMR.

For the spectroscopic identification of intermediates in the CLE reactions in an aprotic medium, we performed ^{31}P NMR monitoring of the reaction of μ-chloride dimer (R_C)-**1a** with phosphine **HL**[10]. Strong coordination of phosphine **HL**[10] and primary amine **HL**[1] that is released in the reaction to the starting *CN*-palladacycle and the resulting *PC*-palladacycles suggests the compositions of the reaction mixtures presented in Scheme 17.

All these species were identified by ^{31}P NMR spectroscopy based on the parameters of the known compounds, the compounds prepared in the present study,

Scheme 17



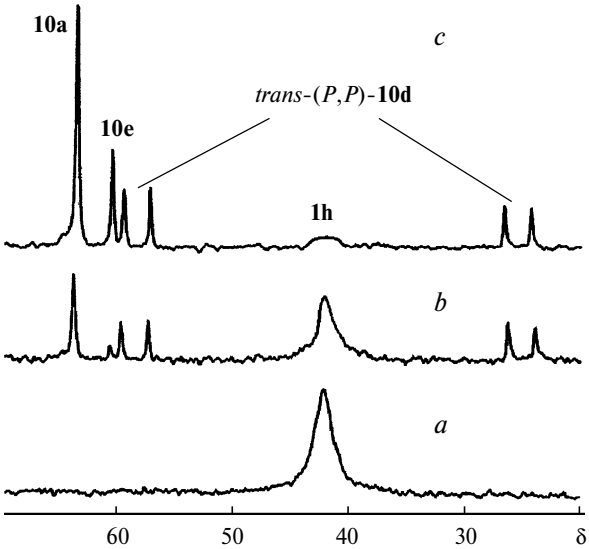


Fig. 1. ^{31}P NMR identification of *P*-containing complexes in the (R_C)-**1a**/**HL**^{10} system in the initial (1 h, *a*), intermediate (54 h, *b*), and final (524 h, *c*) steps.

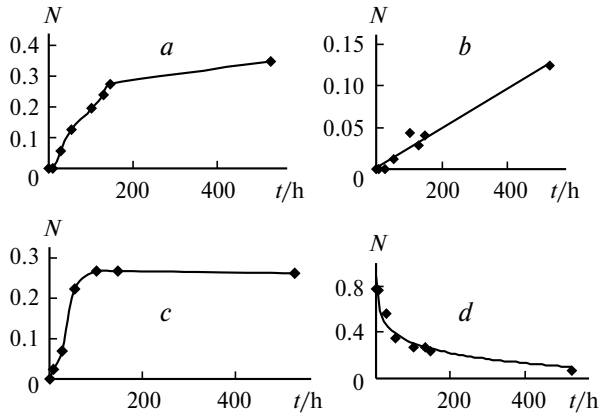


Fig. 2. Dynamics of changes with time of the percentage of *P*-containing species in the reaction mixture: dimer **10a** (*a*), its adducts with amine **10e** (*b*) and phosphine **10d** (*c*), and the adduct of the *CN*-palladacycle with phosphine **1h** (*d*).

authentic compounds generated *in situ*, or their close analogs (Fig. 1).

The signals at δ −7.2 (s) and 63.5—63.8 (br.s) were assigned to phosphine **HL**^{10} and *PC*-dimer **10a**, respectively, based on their known characteristics (δ −7.33 and 63.78).[41,52] The signals of the mononuclear adduct of the *PC*-palladacycle with α-Bu^t-benzylamine (S_P,R_C)-**10e** (δ 60.4—60.8) are similar to the corresponding parameters of the *cis*/*trans*(*P*,*N*) isomers of this complex generated *in situ* by the reaction of dimer *rac*-**10a** with amine *rac*-**HL**^{1} (δ 59.9 and 60.7). The characteristic pair of doublets at δ 58.3—58.7 and 25.3—25.6 with the constant $^2J_{P,P} \approx 373$ Hz (see Ref. 53) was assigned to the adduct of the *PC*-dimer with phosphine **HL**^{10} (**10d**) having the *trans*(*P*,*P*) configuration. The fact that the low-field doublet belongs to the *PC*-palladacycle is evident from the similarity between its chemical shift and the parameters of dimer **10a** (δ 63.8)[41,52] and its PPh_3 derivative (δ 58.3; $^2J_{P,P}$ = 399 Hz).[41] The broad signal of the phosphine adduct of the *CN*-palladacycle (δ 41.6—42.7) was identified based on the chemical shift of authentic complex **1h**, which was synthesized (δ 44.7) or generated *in situ* by the reaction of dimer *rac*-**1a** with phosphine **HL**^{10} (δ 41.9). A strong broadening of the signals in the spectra of adduct **1h** (Δδ 230—260 Hz) can be attributed to the exchange processes and hindered rotation of bulky monodentate phosphine **HL**^{10} about the Pd←P and P—C^{ipso} bonds (the Tolman cone angle is 190°).[54]

The validity of the above assignments is confirmed by the dynamics of changes with time of the population of the CLE participants in the (R_C)-**1a**/**HL**^{10} system (Fig. 2).* In the course of the reaction, the fractions of *PC*-dimer

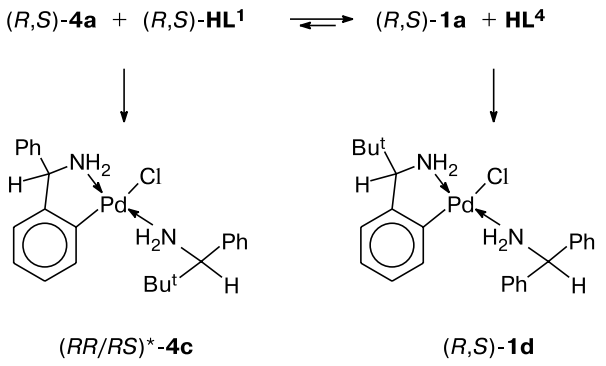
* The concentrations of the complexes were calculated from their contributions to the total intensity of all signals of *P*-containing species taking into account that the total content of ^{31}P nuclei in the reaction mixture is kept constant.

10a and its adducts with amine $\mathbf{HL^1}$ (**10e**) and phosphine $\mathbf{HL^{10}}$ (**10d**) increase (Fig. 2, *a*—*c*), whereas the percentage of the adduct of the *CN*-dimer with phosphine $\mathbf{HL^{10}}$ (**1h**) in the reaction mixture decreases (Fig. 2, *d*).

The similar intermediate adducts [(η^2-$\mathbf{L^1}$)Pd(κ^1-$\mathbf{HL^{10}}$)Br] (**1j**) and [(η^2-$\mathbf{L^{10}}$)Pd (κ^1-**HL**)Br] (**HL** = $\mathbf{HL^1}$ (**10f**) or $\mathbf{HL^{10}}$ (**10g**)) were also identified by spectroscopic monitoring of CLE with μ-bromide reagent (R_C)-**1b**/$\mathbf{HL^{10}}$. Complex *rac*-**1j** was synthesized independently.

The intermediate formation of the mononuclear adducts [(C^N)Pd(κ^1-**HL**)Cl] was detected by ^{1}H NMR spectroscopy only in the reactions with primary benzylamines. One of these adducts (**4c**) was synthesized independently (Scheme 18). Coordination of primary benzylamines to the metal atom in alternative reactions, *viz.*, the forward reaction (*rac*-**4a**/*rac*-$\mathbf{HL^1}$) and the backward reaction (*rac*-**1a**/$\mathbf{HL^4}$), is confirmed by the coordination shifts of the signals of the amines and the diastereotopicity of the protons of the NH_2 group in the spectra of adducts **4c** and **1d**, respectively.

Scheme 18



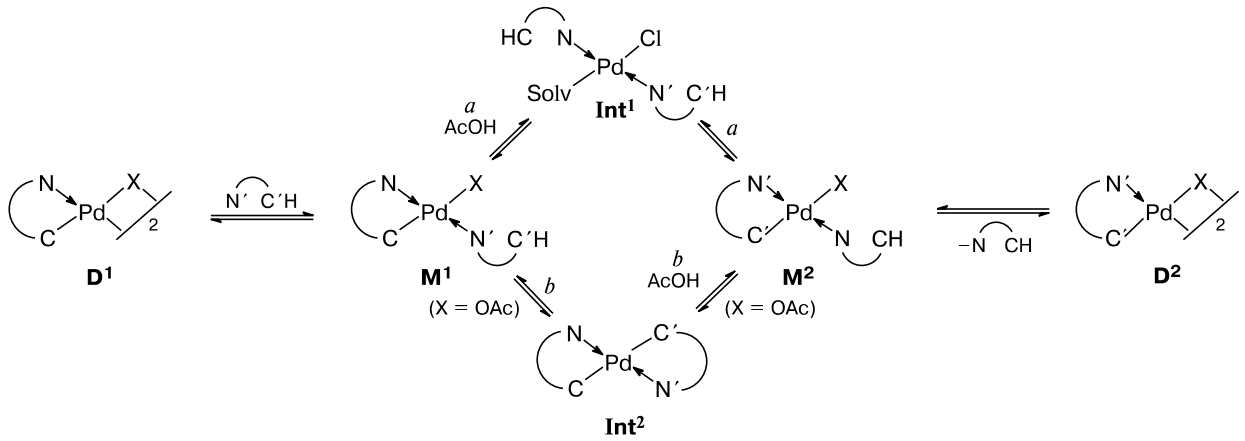
Mechanistic aspects of cyclopalladated ligand exchange

The dissociative mechanism of this reaction in an acidic medium is commonly recognized. It is assumed that all steps of this reaction are reversible,[31,32,38,39,55—58] and the position of the equilibrium between two palladacycles is determined by relative stability of two σ-Pd—C bonds to acidolysis.[32,57] Two known schemes of the reaction differ only in the structure of the key intermediate, which is either a coordination compound with two monodentate ligands ($\mathbf{Int^1}$)[38] or a bis(chelate) *spiro* complex ($\mathbf{Int^2}$) with two metallacycles[32] (Scheme 19).

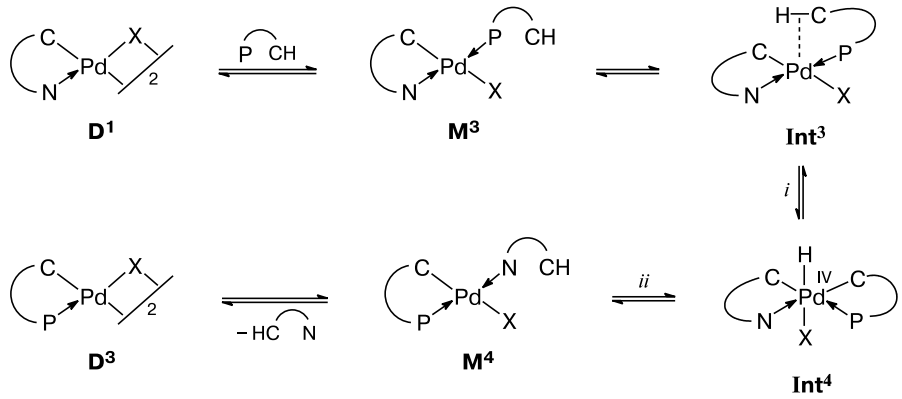
The first version (Scheme 19, path *a*) is based on the data on the kinetics and thermodynamics of CLE and experiments with *D*-labeled models.[31,38,55] This is stereochemically confirmed by the absence of asymmetric induction in the reactions with optically active palladacycles, which has been noted earlier[15,17] for a system with an *N*-donor as well as was observed in our study for the reactions with *N*-, *S*-, and *P*-donor ligands. The second version (path *b*) seems to be hardly probable because it is inconsistent with both the stereochemical criterion (C—H bond activation in the presence of a chiral palladacycle should be accompanied by a pronounced asymmetric induction) and the known conditions of the formation of $\mathbf{Int^2}$-type *spiro* complexes (see Refs 59—61).

It is evident that the mechanisms assumed for CLE in acidic media are inapplicable to analogous processes in aprotic media. The characteristic features of "acid-free" CLE, which we revealed experimentally, provide evidence for a radically different pathway of this reaction. High asymmetric induction under these conditions is a stereochemical evidence for the retention of the starting palladacycle in the step of formation of a new palladacycle. The progress of the reaction is determined by the relative ability of two ligands to undergo cyclometallation, *P*-donor substrates being preferable, whereas tertiary

Scheme 19



Scheme 20



i is the oxidative addition of the C—H bond; *ii* is reductive elimination.

benzylamines and thioamides are nonreactive. In this step, only some speculations about the probable pathway of CLE involving phosphine ligands in aprotic solvents can be made (Scheme 20).

Like the pathways proposed for acidic media (see Scheme 19), the reaction in an aprotic medium involves the interconversions of dimeric and monomeric species $\mathbf{D^1} \rightarrow \mathbf{M^3}$ and $\mathbf{M^4} \rightarrow \mathbf{D^3}$ as the first and final steps, respectively (Scheme 20); the key intermediates should be radically different. The commonly accepted cyclometallation mechanisms[46,48,62,63] suggest that the C—H bond activation should be preceded by its agostic interactions with the metal atom (**Int^3**); the subsequent oxidative addition of the C—H bond to the metal atom can lead to the closure of the phosphapalladacycle in the form of Pd^{IV} hydride (**Int^4**). Compounds of Pd^{IV} are well known, including the structures with palladacycles.[64—66] The reaction comes to an end after reductive elimination to form a C—H bond.

In addition to the spectroscopic identification of the reaction participants (see Scheme 17), there are spectroscopic arguments for the formation of intermediate **Int^3**. A decrease in the distance between the metal atom in the axial position and the *o*-Me group of one of the *P*-tolyl fragments in monodentate phosphine **HL^{10}** in adducts **1h** and **1j** is confirmed by ^{1}H NMR spectroscopy. Of two signals for the protons of the diastereotopic *o*-Me groups (δ 2.38 and 2.66; 2.42 and 2.83), the former signal retains its position typical of free phosphine (δ 2.38), whereas the latter signal is shifted downfield (Δδ ~0.27 and 0.41, respectively) due to the anisotropy of the metal atom (which is more pronounced in the case of bromide adduct **1j**). This provides conditions for the subsequent agostic interaction between this C—H bond and the palladium atom.

We failed to grow crystals of the adduct of *CN*-dimer (S_C)-**1a** with phosphine **HL^{10}** (**1h**) suitable for X-ray diffraction. However, we used its analog, *viz.*, [(η^2-L^3)Pd(κ^1-**HL^{10}**)Cl] (**3c**), for this purpose. The molecular structure

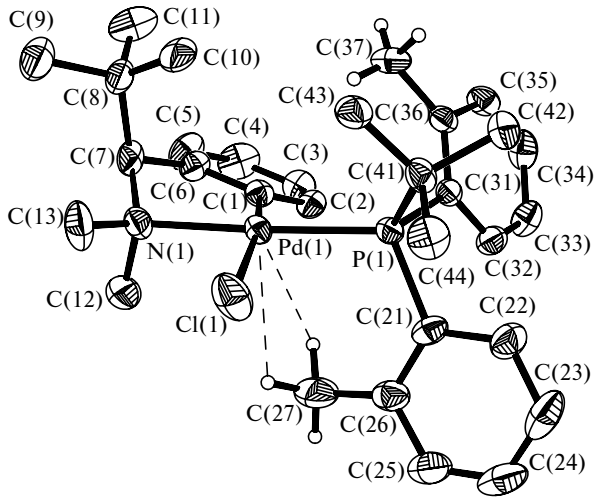


Fig. 3. Molecular structure and the atomic numbering scheme for phosphine adduct (S_C)-**3c**. All atoms except for the H atoms of the *ortho*-methyl groups are omitted.

of **3c** is shown in Fig. 3. Principal structural parameters of complex (S_C)-**3c** are similar to the corresponding parameters typical of phosphine adducts of *ortho*-palladated tertiary amines.[18,43,44,67,68] This is true for the principal bond lengths, the degree of puckering of the palladacycle (26.28°), and a tetrahedral distortion of the coordination sphere (8.0°), as well as for the total Λλ(S_C) stereochemistry of the complex.

The most important result of X-ray diffraction study of adduct (S_C)-**3c** is corroboration of shortened contacts of two protons of the *o*-Me group (C(27)) of one of the *P*-tolyl substituents with the palladium atom (2.63(8) and 2.67(9) Å; the sum of van der Waals radii of these atoms is 3.1 Å),[69] whereas the Pd···H distances for the *o*-Me protons of the second *P*-tolyl group is longer than 3.15 Å. The orientation of the first P(Tol-*o*) substituent is optimal for the secondary interaction in the axial position. The aromatic ring is virtually coplanar to the Pd←P bond. The

$PdPC_{ipso}C_{ortho}(Me)$ torsion angle is 19.9(6)° (*cf.* the angle of 59.7(6)° for the second *P*-tolyl substituent). The attractive character of the secondary interaction is evidenced by a noticeable decrease in the $PdPC_{ipso}$(Tol-*o*) bond angle to 112.7(2)° for the "axial" P(Tol-*o*) group compared to 119.0(2)° for the second "skewed" *P*-tolyl substituent. It should be emphasized that the shortened distance to the metal atom was observed for this of two diastereotopic *P*-tolyl groups (*pro*(R_P)-(Tol-*o*)), which is subjected to cyclopalladation in the course of asymmetric CLE in the presence of the *CN*-palladacycle having the (S_C) configuration. This model accounts for the stereochemical directionality of CLE in the (S_C)-**1a**/**HL**[10] system, in which a high optical yield of the phosphapalladacycle was achieved.

To conclude, we developed the asymmetric version of CLE and established the factors responsible for its efficiency. The key role of an aprotic medium was established to enable the prevention of premature destruction of the starting *CN*-palladacycle, which serves simultaneously as the reagent and the chirality inductor. It was demonstrated that the easier C—H bond activation in the substrate compared to the ligand corresponding to the reagent is the main condition for an efficient shift of the equilibrium between two palladacycles toward the target product. A cyclopalladated reagent characterized by an optimal combination of the reactivity and the ability for chiral recognition was found. It was demonstrated for the first time that both the efficiency and enantioselectivity of CLE can be substantially increased by replacing the bridging chloride ligand in the dimeric cyclopalladated reagent by bromide. The CLE reactions not only at room temperature but also at negative temperatures were carried out for the first time.

Our results shatter the myth that CLE cannot be in principle performed in an acid-free medium.[15,32,39,55,58] This delusion is strange, the more so that the transfer of cyclometallated ligands in aprotic media in reactions of pincer *PCP*-complexes of other transition metals[70,71] and in transmetallation[57] is well known.

Shortly after our preliminary publication on the development of the asymmetric version of CLE,[29] this method was applied[72] to the efficient (*ee* 78—95%) generation of planar chirality of *PC*-palladacycles with the use of a bulky planar chiral cobalticene reagent. This result demonstrates a high potential of the above-described method and broad prospects for its further improvement.

Experimental

The ^1H and $^{31}P\{^1H\}$ NMR spectra were recorded on Varian VXR-400 and Bruker DPX-400 spectrometers operating at 400 and 169.1 MHz, respectively, in $CDCl_3$ at room temperature. The chemical shifts in the ^1H and ^{31}P NMR spectra were measured relative to Me_4Si (internal standard) and H_3PO_4 (external standard), respectively. The assignments of the signals were made with the use of homonuclear double resonance. The melting points were measured using the melting point indicator EM-MGU No. 49 in a sealed capillary tube. The specific rotation was measured on an automated VNIEKI-prodmash A1-EPO polarimeter at the sodium *D* line. All manipulations with free phosphines (except for PPh_3) were carried out under argon in anhydrous solvents with the use of the Schlenk technique. The course of the reactions was monitored and the purity of the compounds was checked by TLC on Silufol UV-254. Flash chromatography or dry column chromatography[73] on Silpearl silica gel was used for isolation of the resulting complexes.

The solvents were purified according to standard procedures.[42] The reagents $PdCl_2$, $Pd(OAc)_2$, KPF_6 (Aldrich), and $AgNO_3$ were used without additional purification; Li_2PdCl_4 was synthesized according to a known procedure.[45] Ethylenediamine (high-purity grade) was dried and distilled over KOH; triphenylphosphine was purified by double recrystallization from a benzene—hexane mixture; (*S*)-α-methylbenzylamine ($[\alpha]_D$ −41.0) was purified by distillation. (1*R*,2*R*)-1,2-Diphenylethane-1,2-diamine (*ee* 99%, Aldrich) and (*S*)-proline (high-purity grade) with $[\alpha]_D$ −53.0 (*c* 0.5, 0.5N HCl) were used without additional purification; *N*-acetyl-(*R*)-leucine was prepared according to a known procedure.[74] Sodium and potassium (*S*)-prolinates were synthesized by treatment of (*S*)-proline with an equimolar amount of NaOH or KOH in methanol at 20 °C. After removal of the solvent, the residue was thoroughly dried *in vacuo*.

Racemic α-*tert*-butylbenzylamine **HL**[1],[75] its (*R*)- and (*S*)-enantiomers,[37,76] (*R*)-*N*-methyl-α-*tert*-butylbenzylamine (*R*)-**HL**[2],[77] (*S*)-*N*,*N*-dimethyl-α-*tert*-butylbenzylamine, (*S*)-**HL**[3],[37] (*S*)-*N*,*N*-dimethyl-α-methylbenzylamine (*S*)-**HL**[7],[78] (*S*)-*N*-isopropyl-α-methylbenzylamine (*S*)-**HL**[6],[43] benzhydrylamine **HL**[4],[79] *N*,*N*-dimethylbenzhydrylamine **HL**[8],[50] di-*tert*-butyl(ferrocenylmethyl)phosphine **HL**[9],[40] *tert*-butyl-di-*ortho*-tolylphosphine **HL**[10],[80] and *N*-thiopivaloylpiperidine **HL**[11] (see Ref. 81) were prepared according to known procedures.

rac-Di-μ-chlorobis[2-{1-amino-2,2-dimethylpropyl}phenyl-*C*,*N*]dipalladium(II) (**1a**)[44], (R_C)-**1a** (see Ref. 29) and (S_C)-**1a**,[29,82] (R_CS_N)-di-μ-chlorobis{2-[2,2-dimethyl-1-(methylamino)propyl]phenyl-*C*,*N*}dipalladium(II) ((R_CS_N)-**2a**),[77] (S_C)-di-μ-chlorobis[2-(1-dimethylamino-2,2-dimethylpropyl)phenyl-*C*,*N*]dipalladium(II) ((S_C)-**3a**),[37] (S_C)-di-μ-chlorobis[2-{1-aminoethyl}phenyl-*C*,*N*]dipalladium(II) ((S_C)-**5a**)[83], (S_CR_N)-di-μ-chlorobis[2-{1-(isopropylamino)ethyl}phenyl-*C*,*N*]dipalladium(II) ((S_CR_N)-**6a**),[84] and (S_C)-di-μ-chlorobis[2-{1-(dimethylamino)ethyl}phenyl-*C*,*N*]dipalladium(II) ((S_C)-**7a**)[85] were synthesized according to known procedures.

Racemic di-μ-chlorobis[2-{1-(amino)benzyl}phenyl-*C*,*N*]dipalladium(II) (*rac*-4a). A mixture of $Pd(OAc)_2$ (140.0 mg, 0.6168 mmol) and benzhydrylamine (114.4 mg, 0.6168 mmol) in benzene (4 mL) was stirred at 60 °C for 9 h. Then LiCl (136.0 mg, 3.084 mmol) was added and the mixture was stirred for 1 h. The precipitate that formed was filtered off, washed with benzene and chloroform, and purified by dry column chromatography (h = 2 cm, d = 2.5 cm, benzene—acetone mixtures in ratios from 20 : 1 to 1 : 20 as the eluent). Dimer **4a** was obtained in a yield of 127.5 mg (64%). M.p. (with decomp.) 239—241 °C, R_f 0.37 (benzene—acetone, 10 : 1). Found (%): C, 47.6; H, 3.7; N, 4.1. $C_{26}H_{24}Cl_2N_2Pd_2$. Calculated (%): C, 48.2; H, 3.7; N, 4.3.

Racemic chloro[2-{1-(amino)benzyl}phenyl-*C*,*N*](triphenylphosphine)palladium(II) (*rac*-4b). A mixture of dimer *rac*-**4a**

(14.1 mg, 0.0217 mmol) and PPh_3 (11.5 mg, 0.044 mmol) in benzene (4 mL) was stirred at 20 °C for 1 h and concentrated. Complex ***rac*-4b** was precipitated with hexane. Adduct **4b** was obtained in a yield of 21.6 mg (85%) as a pale-yellow powder. M.p. (with decomp.) 157—159 °C, R_f 0.31 (benzene—acetone, 10 : 1). Found (%): C, 63.73; H, 4.72; N, 2.21. $C_{31}H_{27}ClNPPd$. Calculated (%): C, 63.49; H, 4.64; N, 2.39. ^{31}P NMR, δ: 40.99 (s). ^1H NMR, δ: signals for the protons of palladacycle: 3.897 (m, 1 H, NH_{eq}, $^3J_{H,P}$ = 3.5 Hz, $^2J_{H,H}$ = 10.5 Hz, $^3J_{HN,CH}$ = 6.4 Hz); 4.570 (m, 1 H, NH_{ax}, $^3J_{H,P}$ = 3.5 Hz, $^2J_{H,H}$ = 10.5 Hz, $^3J_{HN,CH}$ = 6.4 Hz); 5.537 (ddd, 1 H, α-CH, $^4J_{H,P}$ = 4.5 Hz, $^3J_{HC,NH}$ = 6.4 Hz); 7.34—7.50 (group of m, 5 H, α-Ph; 9H, *m*- and *p*-H of PPh_3); 6.40—6.46 (m, 2 H, C(5)H, C(6)H of the C_6H_4 fragment); 6.774 (m, 1 H, C(4)H, $^3J_{H,H}$ = 7.8 Hz); 6.583 (d, 1 H, C(3)H, $^3J_{H,H}$ = 7.2 Hz); signals of PPh_3: 7.33—7.50 (m, 9 H, H_m and H_p, overlap with the signals for the protons of the α-Ph group); 7.745 (m, 6 H, H_o, $^3J_{H,P}$ = 11.2 Hz).

Racemic di-μ-chloro-bis(*N*-thiopivaloylpiperidin-2-yl-*C*,*S*)dipalladium(II) (*rac*-11a). A mixture of $PdCl_2$ (47.8 mg, 0.270 mmol) and *N*-thiopivaloylpiperidine (50.0 mg, 0.270 mmol) in methanol (6 mL) was stirred at 50 °C for 6 h. The precipitate that formed was filtered off, extracted with dichloromethane, and purified by flash column chromatography (*h* = 3 cm, *d* = 1.5 cm, a benzene—acetone mixture, 5 : 1, as the eluent). After recrystallization from a dichloromethane—diethyl ether mixture, dimer **11a** was obtained in a yield of 82.7 mg (94%) as a pale-yellow amorphous powder, m.p. (with decomp.) 210—212 °C, R_f 0.6 (benzene—acetone, 5 : 1). Found (%): C, 36.66; H, 5.62; N, 3.90. $C_{20}H_{36}Cl_2N_2Pd_2S_2$. Calculated (%): C, 36.82; H, 5.56; N, 4.29.

Racemic chloro(*N*-thiopivaloylpiperidin-2-yl-*C*,*S*)(pyridine-*N*)palladium(II) (*rac*-11b). An excess of pyridine (121.2 mg, 1.532 mmol) in benzene (20 mL) was added to a suspension of dimer *rac*-**11a** (52.0 mg, 0.0766 mmol). The reaction mixture was stirred at 20 °C for 0.5 h, filtered, and concentrated. The residue was recrystallized from a dimethylchloromethane—hexane mixture on cooling to −70 °C. Complex *rac*-**11b** was obtained in a yield of 51.9 mg (81%); m.p. (with decomp.) 197—198 °C. Found (%): C, 43.35; H, 5.73. $C_{15}H_{23}ClN_2PdS$. Calculated (%): C, 43.07; H, 5.54. ^1H NMR, δ: signals of the palladacycle: 1.433 (s, 9 H, Bu^t); 1.55—2.00 (group of m, 5 H, β-H_{ax}, 2β′-H, 2γ-H); 2.824 (m, 1 H, β-H_{eq}, $^2J_{H,H}$ = 13.5 Hz); 3.218 (ddd, 1 H, α′-H_{ax}, $^2J_{H,H}$ = 13.0 Hz, $^3J_{α\text{-}H_{ax},β\text{-}H_{ax}}$ = 9.4 Hz, $^3J_{α\text{-}H_{ax},β\text{-}H_{eq}}$ = 2.7 Hz); 4.433 (m, 1 H, α′-H_{eq}, $^2J_{H,H}$ = 13.0 Hz); 4.771 (dd, 1 H, α-H_{ax}, $^3J_{α\text{-}H_{ax},β\text{-}H_{ax}}$ = 12.0 Hz, $^3J_{α\text{-}H_{ax},β\text{-}H_{eq}}$ = 2.1 Hz); signals of coordinated pyridine: 7.328 (t, 2 H, β-H, $^3J_{H,H}$ = 6.6 Hz); 7.737 (t, 1 H, γ-H, $^3J_{H,H}$ = 7.5 Hz); 8.786 (d, 2 H, α-H, $^3J_{H,H}$ = 5.0 Hz).

Racemic di-μ-bromo-bis[2-{1-amino-2,2-dimethylpropyl}phenyl-*C*,*N*]dipalladium(II) (*rac*-1b). A solution of μ-chloride dimer *rac*-**1a** (43.7 mg, 0.0718 mmol) and a 20% excess of sodium bromide (17.3 mg, 0.173 mmol) in methanol (6 mL) was stirred for 5.5 h. Then the reaction mixture was concentrated to dryness, the residue was dissolved in chloroform and extracted with water (3×10 mL), the organic layer was dried over sodium sulfate, the solvent was removed, and the residue was recrystallized from a $CHCl_3$—hexane mixture. Dimer *rac*-**1b** was obtained in a yield of 24.0 mg (48%) as a yellow amorphous precipitate. M.p. 184—186 °C, R_f 0.37 (benzene—acetone, 20 : 1; twofold elution). Found (%): C, 37.91; H, 4.49; N, 4.20. $C_{22}H_{32}Br_2N_2Pd_2$. Calculated (%): C, 37.90; H, 4.63; N, 4.02. ^1H NMR, δ: 1.22 (s, 9 H, α-Bu^t); 2.94, 3.10, 3.56, and 3.94 (all br.m, 3 H, NH_2, α-CH); 6.84—6.97 (m, 3 H, H(3), H(4), H(5)); 7.41 (br.d, 1 H, H(6)).

(*R*,*R*)-Di-μ-bromobis[2-{1-amino-2,2-dimethylpropyl}phenyl-*C*,*N*]dipalladium(II) ((*R*,*R*)-1b). A mixture of μ-chloride dimer (*R*)-**1a** (79.5 mg, 0.1307 mmol) and sodium bromide (26.9 mg, 0.2614 mmol) in methanol (10 mL) was stirred under argon for 2 h, concentrated *in vacuo*, and then extracted with a dichloromethane—water mixture. The organic extract was dried over sodium sulfate. Dimer (*R*)-**1b** was obtained in a yield of 70.7 mg (78%); m.p. (with decomp.) 223—225 °C, R_f 0.21 (diethyl ether—hexane, 1 : 1). The ^1H NMR spectrum of dimer (*R*,*R*)-**1b** is identical to that given above for the racemate.

(*R*,*S*)-Bromo[2-{1-amino-2,2-dimethylpropyl}phenyl-*C*,*N*](triphenylphosphine)palladium(II) (*rac*-1c). A solution of a mixture of μ-bromide dimer *rac*-**1b** (5.0 mg, 0.0072 mmol) and triphenylphosphine (4.2 g, 0.0157 mmol) in toluene (4 mL) was stirred at room temperature for 6 h. The reaction mixture was concentrated and the residue was recrystallized from a mixture of toluene and petroleum ether. The precipitate that formed was filtered off, washed with petroleum ether, and dried. Adduct *rac*-**1c** was obtained in a yield of 7.1 mg (81%) as colorless crystals, m.p. 224—225 °C, R_f 0.26 (diethyl ether—hexane, 1 : 1, twofold elution). Found (%): C, 57.26; H, 5.07; N, 2.20. $C_{29}H_{31}BrNPPd$. Calculated (%): C, 57.02; H, 5.12; N, 2.29. ^{31}P NMR, δ: 40.7 (s). ^1H NMR, δ: signals of the palladacycle: 1.31 (s, 9 H, α-Bu^t); 3.81 (br.dd, 1 H, NH_{eq}, $^2J_{H,NH}$ = 9.6 Hz, $^3J_{H,P}$ = 2.2 Hz); 3.93 (br.ddd, 1 H, NH_{ax}, $^2J_{H,NH}$ = 9.6 Hz, $^3J_{HN,CH}$ = 6.7 Hz, $^3J_{H,P}$ = 4.0 Hz); 4.06 (dd, 1 H, α-CH, $^3J_{HC,NH}$ = 6.1 Hz, $^4J_{H,P}$ = 6.1 Hz); 6.39 (br.ddd, 1 H, H(6), $^3J_{6,5}$ = 7.6 Hz, $^3J_{H,P}$ = 6.1 Hz, $^4J_{6,4}$ = 1.0 Hz); 6.44 (t, 1 H, H(5), $^3J_{5,6}$ = 7.6 Hz, $^3J_{5,4}$ = 6.8 Hz); 6.83 (dd, 1 H, H(4), $^3J_{4,5}$ = 6.8 Hz, $^3J_{4,3}$ = 7.6 Hz); 7.02 (d, 1 H, H(3), $^3J_{3,4}$ = 7.6 Hz); signals of PPh_3: 7.34—7.44 (m, 9 H, H_m, H_p); 7.73 (m, 6 H, H_o, $^3J_{H,P}$ = 11.2 Hz).

(*R*)-Bromo[2-{1-amino-2,2-dimethylpropyl}phenyl-*C*,*N*](triphenylphosphine)palladium(II) ((*R*)-1c). A solution of a mixture of dimer (*R*)-**1b** (58.0 mg, 0.083 mmol) and triphenylphosphine (47.9 mg, 0.1828 mmol) in benzene (5 mL) was stirred at 20 °C for 1 h, the solvent was removed, and the complex was purified by dry column chromatography (*h* = 2 cm, *d* = 1.5 cm, benzene—acetone mixtures, from 1 : 0 to 10 : 1). Adduct (*R*)-**1c** was isolated in a yield of 71.0 mg (85%) as a colorless powder, m.p. (with decomp.) 222—224 °C, R_f 0.51 (benzene—acetone, 7 : 1), $[\alpha]_D$ +51 (*c* 0.4, CH_2Cl_2). Found (%): C, 56.80; H, 5.32; N, 2.09. $C_{29}H_{31}BrNPPd$. Calculated (%): C, 57.02; H, 5.12; N, 2.29.

Cyclopalladated ligand exchange. The structures of the CLE products were confirmed by a comparison of their spectroscopic characteristics (^1H and ^{31}P NMR) with the characteristics published earlier. The intermediate adducts of the *CN*- and *PC*-dimers with the substrates were identified by spectroscopy based on the characteristics of the corresponding species, which were either prepared independently or generated *in situ* by the reaction of the corresponding dimeric cyclopalladated complex with a stoichiometric amount of the ligand in benzene (20 °C, 0.5—1 h).

Cyclopalladated ligand exchange reactions with benzylamines. ***A.*** A solution of amine **HL**[8] (92.0 mg, 0.435 mmol) in toluene (5 mL) and glacial acetic AcOH (10 mL) was added to a suspension of dimer (S_C)-**7a** (126.3 mg, 0.2176 mmol) in toluene (5 mL). The reaction mixture was stirred at 50 °C for 17 h,

Pd^0 was removed by filtration, and the filtrate was concentrated to dryness. The residue was dissolved in CH_2Cl_2 (10 mL), the solution was vigorously shaken with 1 *M* aqueous HCl (2×5 mL), and the combined aqueous extracts were extracted with dichloromethane. The organic layer was dried over Na_2SO_4, the solvent was removed *in vacuo*, and the dimeric complexes were separated by flash column chromatography (h = 16 cm, d = 2 cm; benzene—acetone mixtures, from 80 : 1 to 10 : 1). Dimer *rac*-**8a** (*ee* <2%), m.p. (with decomp.) 195—196 °C, was isolated in a yield of 63.7 mg (42%). Reagent (S_C)-**7a**, m.p. (with decomp.) 182—183 °C; $[\alpha]_D$ +73.4 (*c* 0.36, benzene), was recovered in a yield of 39.5 mg (54%). For dimers **8a** and **7a**, R_f are 0.53 and 0.59 (diethyl ether—heptane, 3 : 1), respectively.

B. Analogously, after chromatography (h = 10.5 cm, d = 1.2 cm) of the mixture prepared by the reaction of dimer (S_C)-**1a** (52.4 mg, 0.0861 mmol) with amine **HL[8]** (36.4 mg, 0.172 mmol) at 50 °C (5.5 h), dimer *rac*-**8a** ($[\alpha]_D$ <5, *ee* <4%), m.p. (with decomp.) 195—196 °C, and reagent (S_C)-**1a**, m.p. (with decomp.) 217—219 °C; $[\alpha]_D$ +146 (*c* 0.4, CH_2Cl_2—pyridine), were isolated in yields of 25.4 (42%) and 21.0 mg (69%), respectively. For dimers **1a** and **8a**, R_f are 0.44 and 0.80 (benzene—acetone, 10 : 1), respectively.

C. A mixture of racemic dimer **4a** (17.8 mg, 0.0275 mmol) and amine **HL[1]** (9.0 mg, 0.0551 mmol) in toluene (5 mL) was stirred at 20 °C for 75 days, the solvent was removed *in vacuo*, a solution of the residue in dichloromethane (5 mL) was treated with 1 *M* HCl (2×5 mL), and the aqueous extracts were extracted with dichloromethane. The organic layer was dried over Na_2SO_4, the solvent was removed, and the residue was subjected to dry column chromatography (h = 2 cm, d = 1 cm; benzene—acetone mixtures, from 20 : 1 to 1 : 1). Since dimers **1a** and **4a** have similar chromatographic mobilities (R_f 0.44 and 0.39, respectively; benzene—acetone, 10 : 1), the composition of the reaction mixture was estimated after the transformation of the dimers into the mononuclear phosphine derivatives by the reaction with PPh_3 (15.9 mg, 0.0606 mmol) in benzene (2 mL) at 20 °C (30 min). ^{31}P NMR spectroscopy revealed the presence of two phosphine adducts, **1g** and **4b** (δ 39.68 and 41.16, respectively), in a ratio of 1 : 4.6, which corresponds to the degree of conversion of 18%. The ^1H NMR spectra of these adducts are identical to the spectra of individual adducts **1g** [44] and **4b** (see below).

D. In the reaction of dimer (S_C)-**1a** (60.0 mg, 0.0986 mmol) with amine **HL[4]** (36.1 mg, 0.197 mmol) under the analogous conditions (20 °C, 37 days; 50 °C, 70 h) followed by treatment with PPh_3 (56.9 mg, 0.2169 mmol), the formation of dimer **4a** (based on its adduct **4b**) was not observed. The ^{31}P NMR spectrum shows one signal (δ 39.65) corresponding to the adduct of the starting *CN*-dimer (S_C)-**1a** with phosphine PPh_3, *viz.*, (S_C)-**1g**.[44] ^1H NMR of intermediate adduct (S_C)-**1d** (δ): signals of the palladacycle: 0.856 (s, 9 H, Bu^t); 3.673 (d, 1 H, α-CH, $^3J_{HC,NH_{ax}}$ = 5.7 Hz); 5.400 (br.s, 1 H, NH_{eq}); 2.855 (br.dd, 1 H, NH_{ax}, $^2J_{H,NH}$ = 10.7 Hz, $^3J_{HN,CH}$ = 5.7 Hz); 6.649 (d, 1 H, C(6)H, $^3J_{6,5}$ = 7.4 Hz); 6.608 (dd, 1 H, C(5)H, $^3J_{5,4}$ = 7.3 Hz, $^3J_{5,6}$ = 7.4 Hz); 6.766 (ddd, 1 H, C(4)H, $^3J_{4,3}$ = 7.5 Hz, $^3J_{4,5}$ = 7.3 Hz, $^4J_{4,6}$ = 1.4 Hz); 6.844 (dd, 1 H, C(3)H, $^3J_{3,4}$ = 7.5 Hz, $^4J_{3,5}$ = 1.2 Hz); signals of coordinated amine **HL[4]**: 2.524 (br.s, 1 H, NH^1); 3.214 (br.s, 1 H, NH^2); 5.329 (d, 1 H, α-CH, $^3J_{HC,NH^1}$ = 7.3 Hz); 7.18—7.40 (group m, 10 H, 2 α-Ph).

E. The formation of neither dimer **4a** (R_f 0.60) nor its adduct with amine **HL[5]** (R_f 0.52) was detected by TLC (diethyl ether—hexane, 5 : 1) in the reaction of dimer (S_C)-**5a** (79.5 mg, 0.1517 mmol) with amine **HL[4]** (55.6 mg, 0.303 mmol) in toluene (5 mL) (20 °C, 144 h; 60 °C, 192 h). After chromatography (h = 2 cm, d = 1 cm, benzene—acetone mixtures, from 20 : 1 to 1 : 1) of the reaction mixture containing dimer **5a** (R_f 0.23) and its adduct with amine **HL[4]** (**5c,** R_f 0.39), dimer (S_C)-**5a** was recovered in a yield of 72.5 mg (91%), m.p. (with decomp.) 188—190 °C, $[\alpha]_D$ +21 (*c* 0.25, CH_2Cl_2).

F. A mixture of dimer (S_C)-**5a** (68.4 mg, 0.1306 mmol) and amine *rac*-**HL[3]** (50.0 mg, 0.261 mmol) in acetonitrile (6 mL) was treated with KPF_6 (480.0 mg, 0.2612 mmol). After removal of KCl and stirring (20 °C, 120 h; 50 °C, 48 h), dimer **3a** (R_f 0.79) was not detected by TLC* (benzene—acetone, 10 : 1). After chromatography (h = 3 cm, d = 1.5 cm, benzene—acetone mixtures, from 10 : 1 to 1 : 1) of the reaction mixture containing the starting dimer (S_C)-**5a** (R_f 0.34) and its adduct with amine **HL[3]** (**5b**, R_f 0.46), dimer (S_C)-**5a** was recovered in a yield of 62.0 mg (91%), m.p. (with decomp.) 188—190 °C, $[\alpha]_D$ +23 (*c* 0.25, CH_2Cl_2).

Cyclopalladated ligand exchange reactions with thioamide.

A. A solution of dimer (S_C)-**1a** (56.5 mg, 0.0928 mmol) and thioamide **HL[11]** (36.6 mg, 0.1856 mmol) in a 1 : 1 mixture of toluene and AcOH (6 mL) was stirred at 20 °C for 7 days. The solvent was removed and the residue was subjected to dry column chromatography (h = 2.5 cm, d = 1.5 cm, benzene—acetone mixtures, from 60 : 1 to 1 : 1); *CS*-dimer **11a** and the starting *CN*-dimer (S_C)-**1a** were isolated in yields of 31.0 (49%) and 26.8 mg (47%), respectively. For dimers **11a** and **1a**, R_f are 0.64 and 0.57 (benzene—acetone, 5 : 1), respectively; *CS*-dimer **11a** was identified based on the ^1H NMR spectrum of its d_5-pyridine adduct generated *in situ* (see above).

B. The formation of dimer **11a** in the reaction of dimer (S_C)-**1a** (56.5 mg, 0.0928 mmol) with thioamide **HL[11]** (36.6 mg, 0.186 mmol) in toluene (5 mL) in the absence of AcOH (20 °C, 21 days) was not detected by the TLC method. The solvent was removed, and the residue was treated with a KPF_6 solution (34.2 mg, 0.186 mmol) in MeCN (3 mL). After prolonged stirring at 20 °C for 28 h and at 50 °C for 10 days, neither dimer **11a** nor its adduct with amine **HL[1]** (**11c**) was detected. According to TLC, the reaction mixture contained only the adduct of the starting dimer **1a** and thioamide **HL[11]** (**1e**); R_f 0.38 (benzene—acetone, 5 : 1). ^1H NMR of adduct **1e** (δ): signals of the palladacycle: 1.191 (s, 9 H, Bu^t); 3.912 (d, 1 H, α-CH, $^3J_{HC,NH_{ax}}$ = 5.8 Hz); 4.007 (br.m, 1 H, NH_{eq}); 3.297 (br.m, 1 H, NH_{ax}); 6.932 (m, 3 H, C(4)H—C(6)H); 7.395 (m, 1 H, C(3)H); signals of **HL[11]**: 1.517 (s, 9 H, Bu^t); 4.128 (br.m, 2 H, α-CH_2); 1.75 (group of br.m, 8 H, α′-CH_2, β-CH_2, β′-CH_2, γ-CH_2). ^1H NMR of adduct **11c** (two sets of signals of *Z*/*E* isomers, 3 : 1) (δ, *J*/Hz): signals of the palladacycle: 1.288 and 1.303 (both s, 9 H each, Bu^t); 1.44—1.80 (group of m, 5 H, β-H_{ax}, β′-CH_2, γ-CH_2); 2.625 and 2.700 (both m, 1 H, β-H_{eq}); 3.038 and 3.060 (both m, 1 H, α′-H_{ax}); 4.288 and 4.346 (both br.d, 1 H, α′-H_{eq}, $^2J_{H,H}$ =13.3 Hz); 4.511, 4.527 (dd, 1 H, α-H_{ax}, $^2J_{H,H}$ = 11.6 Hz, $^3J_{\alpha\text{-}H_{ax},\beta\text{-}H_{eq}}$ = 2.4 Hz); signals of **HL[1]**: 0.920 and 0.933 (both s, 9 H, Bu^t); 2.328 and 2.490 (both br.m, 1 H, NH^1); 2.532 and 2.684 (both br.d, 1 H, NH^2); 3.621 and 3.648 (both t, 1 H, α-CH, $^3J_{HC,NH}$ = 4.0 Hz); 7.15—7.34 (group of m, 10 H, Ph).

* To control the course of the reaction by TLC, the sample was treated with a solution of LiCl in acetone.

Cyclopalladated ligand exchange reactions with ferrocenylmethylphosphine. ***A.*** A solution of dimer (S_C)-**3a** (32.0 mg, 0.0481 mmol) and phosphine **HL**[9] (41.3 mg, 0.120 mmol) in toluene (4 mL) was stirred (20 °C, 500 h; 60 °C, 420 h), the solvent was removed, the residue was dissolved in CH_2Cl_2 (6 mL), and the *PC*-palladacycle was twice extracted with an aqueous solution of a 20-fold excess of ethylenediamine (En) as the cationic derivative (see Scheme 15). Dichloromethane was added to the combined aqueous extracts, and the mixture was acidified with 1 *M* HCl to pH 3—4 with cooling and stirring. The aqueous fraction was extracted with dichloromethane (2×10 mL), and the organic layer was washed with water and dried over Na_2SO_4 (*method* **I**).[51] According to TLC, the solution contained trace amounts of dimer **9a** and reagent **3a** (R_f 0.96 and 0.75, respectively; benzene—acetone, 10 : 1). Dry column chromatography (h = 3 cm, d = 2 cm; benzene—acetone mixtures, from 80 : 1 to 10 : 1) of the solution afforded a ~1 : 10 mixture (4.0 mg) of *PC*-dimer **9a** and *CN*-dimer **3a** (the yield of dimer **9a** <1%) and dimer (S_C)-**3a** (20.0 mg, 71%).

B. After the analogous reaction of dimer (R_CS_N)-**2a** (30.8 mg, 0.0484 mmol) with phosphine **HL**[9] (41.3 mg, 0.1200 mmol) in toluene (4 mL), the starting *CN*-dimer **2a**, its adduct with phosphine **2b**, and *PC*-dimer **9a** were detected by TLC (R_f 0.35, 0.63, and 0.77, respectively; diethyl ether—hexane, 3 : 1). After workup of the reaction mixture according to method **I**, dry column chromatography (h = 3 cm, d = 2 cm, benzene—acetone mixtures, from 80 : 1 to 10 : 1) afforded a ~1 : 6 mixture of *PC*-dimer **9a** and the starting reagent **2a** in a yield of 6.0 mg (the yield of **9a** <2%), and dimer **2a** was recovered in a yield of 20.0 mg (81%).

C. A mixture of dimer (R_C)-**1a** (30.7 mg, 0.0504 mmol) and phosphine **HL**[9] (41.3 mg, 0.120 mmol) in toluene (4 mL) was stirred at 20 °C for 306 h. In this step, the predominance of the phosphine adduct of the *CN*-reagent (**1f**) against traces of reagent **1a** and *PC*-dimer **9a** were detected by TLC (R_f 0.66, 0.49, and 0.77, respectively, diethyl ether—hexane, 3 : 1). After heating (60 °C, 96 h), dry column chromatography (h = 2 cm, d = 2 cm, benzene—acetone mixtures, from 30 : 1 to 1 : 30) afforded *PC*-dimer (S_P)-**9a** (*ee* 44%) in a yield of 12.8 mg (26%), and reagent (R_C)-**1a** was recovered in a yield of 21.0 mg (93%); $[\alpha]_D$ −146 (*c* 0.4, CH_2Cl_2-Py).

Cyclopalladated ligand exchange reactions with di-*ortho*-tolyl-*tert*-butylphosphine. ***A.*** A solution of reagent (S_CR_N)-**6a** (69.9 mg, 0.110 mmol) and phosphine **HL**[10] (60.1 mg, 0.220 mmol) in a mixture of toluene and AcOH (1 : 1, 6 mL) was stirred at 60 °C for 12.5 h. The precipitate that formed was filtered off and washed with toluene. Dimer **10a** with *ee* 2.3% (R_P) was obtained in a yield of 51.4 mg (57%). For dimers **10a** and **6a**, R_f are 0.69 and 0.32 (diethyl ether—hexane, 3 : 1), respectively.

B. The analogous reaction of dimer (R_C)-**1a** (60.0 mg, 0.0986 mmol) with phosphine **HL**[10] (53.3 mg, 0.1972 mmol) in an acidic medium (60 °C, 1 h) produced dimer **10a** with *ee* 2% (*S*) in a yield of 57.6 mg (71%). For dimers **1a** and **10a**, R_f are 0.60 and 0.79 (diethyl ether—hexane, 5 : 1), respectively.

C. A solution of *CN*-dimer (S_C)-**3a** (40.6 mg, 0.0611 mmol) and phosphine **HL**[10] (33.0 mg, 0.122 mmol) in toluene (3 mL) was stirred at 20 °C for 33 days. Since dimers **3a** and **10a** have similar chromatographic mobilities (R_f 0.79 and 0.81, respectively; benzene—acetone, 10 : 1), the course of the reaction was monitored by ^{31}P NMR. In this step, *PC*-dimer **10a** was not detected. The spectrum showed signals of the adduct of the *CN*-dimer with phosphine **HL**[10] (**3c,** δ 42.88, br.s) and free phosphine **HL**[10] (δ −7.43, s). After prolonged heating in toluene (60 °C, 240 h), only trace amounts of *PC*-dimer **10a** (δ 63.8) were detected. In the ^{31}P NMR spectrum, the signal of adduct **3c** (was identified based on the ^{1}H and ^{31}P NMR spectra of racemic complex **3c** prepared by the independent synthesis, see below) dominates. Slow evaporation of a solution of the reaction mixture in toluene afforded crystalline adduct (S_C)-**3c** in a yield of 22.8 mg (31%).

D. A solution of dimer (R_CS_N)-**2a** (50.0 mg, 0.079 mmol) and phosphine **HL**[10] (42.4 mg, 0.158 mmol) in toluene (3 mL) was stirred at 60 °C for 132 h. The precipitate that formed was filtered off, washed with benzene and hexane, and dried; *PC*-dimer (S_P)-**10a** with *ee* 8.8% was obtained as an amorphous cream-colored powder in a yield of 5.2 mg (8%). Reagent (R_CS_N)-**2a** was recovered in a yield of 86% (43.3 mg, 0.0680 mmol). For dimers **2a** and **10a**, R_f are 0.45 and 0.85 (benzene—acetone, 7 : 1), respectively.

E. The reaction of dimer (S_CR_N)-**6a** (69.9 mg, 0.110 mmol) with phosphine **HL**[10] (60.0 mg, 0.220 mmol) was performed in toluene (6 mL) (60 °C, 11 h; 20 °C, 72 h). The precipitate that formed was filtered off and washed with toluene; *PC*-dimer (R_P)-**10a** with *ee* 5.5% was obtained in a yield of 51.4 mg (57%). For dimers **6a** and **10a**, R_f are 0.33 and 0.69 (diethyl ether—hexane, 3 : 1), respectively.

F. A mixture of dimer (S_C)-**5a** (66.4 mg, 0.1266 mmol) and phosphine **HL**[10] (68.5 mg, 0.253 mmol) in toluene (4.5 mL) was stirred at 20 °C for 14 days. The precipitate that formed was filtered off and washed with toluene, benzene, and dichloromethane to give 58.9 mg (0.0716 mmol) of *PC*-dimer **10a**. The combined mother liquors were treated with ethylenediamine according to method **I**. Subsequent separation of the mixture of the dimers by dry column chromatography (h = 3 cm, d = 2 cm, a mixture of diethyl ether—hexane as the eluent, from 1 : 10 to 3 : 1) affroded an additional portion of *PC*-dimer **10a** (10.0 mg), and reagent (S_C)-**5a** was recovered in a yield of 21.0 mg (95%). As a result, dimer (R_P)-**10a** with *ee* 13.4% (*R*) was isolated in a yield of 68.9 mg (66%). For dimers **5a** and **10a**, R_f are 0.05 and 0.46 (diethyl ether—hexane, 1 : 1), respectively.

G. Solutions of phosphine **HL**[10] (8.2 mg, 0.0302 mmol) and KPF_6 (11.2 mg, 0.0604 mmol) in MeCN (4 mL) were successively added to a suspension of dimer *rac*-**1a** (9.2 mg, 00151 mmol) in MeCN (1 mL). The reaction mixture was stirred at 20 °C for 45 days and then LiCl (2.6 mg, 0.0604 mmol) was added. After 1 h, the precipitate was filtered off and washed with water. Dimer *rac*-**10a** was obtained in a yield of 7.0 mg (56.5%). For dimers **1a** and **10a**, R_f are 0.15 and 0.46 (diethyl ether—hexane, 1 : 1), respectively.

H. The analogous reaction of dimer *rac*-**1a** (9.5 mg, 0.0156 mmol) with phosphine **HL**[10] (8.4 mg, 0.0312 mmol) and KPF_6 (11.4 mg, 0.0624 mmol) in acetone (3 mL) produced (45 days) dimer *rac*-**10a** in a yield of 6.8 mg (53%).

K. Heating of dimer (R_C)-**1a** (50.0 mg, 0.0822 mmol) with phosphine **HL**[10] (44.4 mg, 0.1644 mmol) in toluene (3 mL) (60 °C, 58 h) afforded a precipitate, which was filtered off and washed with cold hexane to give *PC*-dimer (S_P)-**10a** with *ee* 66% in a yield of 16.2 mg (24%).

L. After treatment of dimer (R_C)-**1a** (52.2 mg, 0.0858 mmol) with phosphine **HL**[10] (46.4 mg, 0.1716 mmol) in toluene (4 mL), the adduct of the *CN* reagent with (**1h**) was detected spectroscopically (^{31}P NMR). The reaction mixture was stirred at 20 °C

for 140 h and concentrated to dryness. The residue was subjected to dry column chromatography (h = 4 cm, d = 2 cm; hexane and hexane—benzene and benzene—acetone mixtures were used as the eluents, gradient elution). Reagent (R_C)-**1a** was recovered in a yield of 18.8 mg (69%). The combined fractions of the eluates containing *PC*-dimer **10a** and its phosphine adduct **10d** were treated with ethylenediamine according to method **I**. The resulting dimer **10a** was purified by dry column chromatography (h = 2.0 cm, d = 3 cm; benzene—acetone mixtures as the eluents, with polarity gradient). Dimer (S_P)-**10a** with *ee* 72% was isolated in a yield of 33.6 mg (48%). Adduct **1h** was identified based on the ^{1}H and ^{31}P NMR spectra of complex *rac*-**1h** (see below). ^{31}P NMR spectrum of intermediate **10e** (adduct of *PC*-dimer **10a** with benzylamine **HL^1**; a 8 : 1 mixture of *Z*/*E* isomers): δ 60.73 (s) and 59.85 (s). ^{31}P NMR spectrum of adduct *trans*-**10d** (δ): 58.66 (d, palladacycle, $^2J_{P,P}$ = 373 Hz); 25.65 (d, phosphine **HL^{10}**, $^2J_{P,P}$ = 373 Hz).

M. In the analogous reaction of dimer (R_C)-**1a** (50.0 mg, 0.082 mmol) with phosphine **HL^{10}** (44.4 mg, 0.164 mmol) in toluene (5 mL) at 20 °C (528 h), reagent (R_C)-**1a** was recovered chromatographically (h = 3 cm, d = 2.5 cm) in a yield of 35.0 mg (50%), and dimer (S_P)-**10a** with *ee* 81% was isolated from the combined eluates according to method **I** in a yield of 20.2 mg (30%).

N. A solution of dimer (R_C)-**1a** (66.9 mg, 0.110 mmol) and phosphine **HL^{10}** (59.5 mg, 0.220 mmol) in toluene (4 mL) was kept at −13 °C for 5.5 months. After the work-up of the reaction mixture according to the above-described procedure, reagent (R_C)-**1a** was recovered in a yield of 40.9 mg (70%), and *PC*-dimer (S_P)-**10a** with *ee* 86.4% was isolated in a yield of 11.5 mg (13%).

O. The reaction of μ-bromide dimer (R_C)-**1b** (50.0 mg, 0.072 mmol) with phosphine **HL^{10}** (38.8 mg, 0.1430 mmol) in toluene (5 mL) at 20 °C (528 h) according to the same procedure produced *PC*-dimer (S_P)-**10b** with *ee* 91% in a yield of 35.3 mg (54%), and reagent (R_C)-**1b** was recovered in a yield of 6.8 mg (62%). ^{31}P NMR of dimer **10b**, δ: 65.06 (br.s).* ^{31}P NMR spectrum of intermediate **1j** (adduct of dimer **1b** with phosphine **HL^{10}**), δ: 42.76 (br.s). ^{31}P NMR spectrum of intermediate *rac*-**10f** (diastereomers of the adduct of *PC*-dimer *rac*-**10b** with benzylamine *rac*-**HL^1**), δ: 61.96 and 60.50 (two singlets, 22 : 1). ^{31}P NMR spectrum of intermediate *trans*-**10g** (δ) (adduct of *PC*-dimer *rac*-**10b** with phosphine **HL^{10}**): 58.64 (d, *PC*-palladacycle, $^2J_{P,P}$ = 373 Hz); 25.60 (d, coordinated phosphine **HL^{10}**).

Synthesis of intermediate mononuclear adducts. Chloro[2-{1-(amino)benzyl}phenyl-*C*,*N*](1-phenyl-2,2-dimethylpropylamine-*N*)]palladium(II) (*rac*-4c). A mixture of racemic dimer **4a** (30.0 mg, 0.0463 mmol) and amine **HL^1** (15.1 mg, 0.0926 mmol) in benzene (7 mL) was stirred at 20 °C for 17 h and concentrated. Then hexane (5 drops) was added until the mixture became turbid. The precipitate that formed upon cooling was filtered off, washed with hexane, and dried *in vacuo*. After additional recrystallization from a benzene—hexane mixture in the presence of 1 equiv. of amine **HL^1**, adduct **4c** was obtained as a colorless amorphous precipitate in a yield of 10.7 mg (24%). M.p. (with decomp.) 189—191 °C, R_f 0.57 (benzene—acetone, 5 : 1)*. Found (%): C, 59.32; H, 6.17; N, 5.62. $C_{24}H_{29}ClN_2Pd$. Calculated (%): C, 59.15; H, 6.00; N, 5.75. ^{1}H NMR of complex **4c** (δ) (two sets of signals of two diastereomers, ~1 : 1): signals of the palladacycle: 3.884 (m, 1 H, α-CH, $^3J_{HC,NH_{ax}}$ = 9.3 Hz); 4.103 (dd, 1 H, α-CH, $^3J_{HC,NH_{ax}}$ = 9.5 Hz, $^3J_{HC,NH_{eq}}$ = 4.0 Hz); 3.154 and 3.417 (both br.s, 1 H each, NH_{ax}); 4.923 and 4.991 (both m, 1 H each, NH_{eq}); 6.62—6.99 (group of m, 8 H, $2C_6H_4Pd$); 7.1—7.4 (group of m, 20 H, α-Ph groups of the palladacycle and amine **HL^1**); signals of coordinated amine **HL^1**: 0.938 and 0.946 (both s, 9 H each, Bu^t); 3.285 (br.d, 1 H, α-CH, $^3J_{HC,NH^1}$ = 9.3 Hz); 1.711, 2.544, 3.095, and 3.285 (group of m, 5 H, 2 NH^1, 2 NH^2 and α-CH).

Chloro[(*R*,*S*)-2-{1-dimethylamino-2,2-dimethylpropyl}phenyl-*C*,*N*](*tert*-butyl-di-*o*-tolylphosphine-*P*)palladium(II) (*rac*-3c). A mixture of dimer *rac*-**3a** (40.0 mg, 0.075 mmol) and phosphine **HL^{10}** (33.0 mg, 0.1504 mmol) in MeCN (8 mL) was stirred at 20 °C for 5 h. The precipitate was filtered off, and the mother liquor was concentrated to dryness. The dry residue was recrystallized from a benzene—hexane mixture. The precipitate was washed with hexane and dried *in vacuo*. Adduct **3c** was obtained as a yellow finely crystalline precipitate in a yield of 22.8 mg (25%). M.p. (with decomp.) 156—158 °C, R_f 0.27 (diethyl ether—hexane, 1 : 1). Found (%): C, 61.43; H, 7.30; N, 2.47. $C_{31}H_{43}ClNPPd$. Calculated (%): C, 61.80; H, 7.19; N, 2.32. ^{31}P NMR, δ: 42.3 (br.s).

Chloro[(*S*)-2-{1-dimethylamino-2,2-dimethylpropyl}phenyl-*C*,*N*](*tert*-butyl-di-*o*-tolylphosphine-*P*)palladium(II) ((*S*)-3c). A solution of dimer (*S*,*S*)-**3a** (20.0 mg, 0.0301 mmol) and phosphine **HL^{10}** (22.8 mg, 0.0843 mmol) in toluene (6 mL) was stirred (20 °C, 6.5 h; 50 °C, 2 h). The reaction mixture was concentrated and treated with heptane. The precipitate that formed was filtered off, washed with heptane, and dried. After repeated recrystallization from a toluene—heptane mixture, adduct (*S*)-**3c** was isolated as a pale-yellow crystalline precipitate in a yield of 8.5 mg (24%). M.p. (with decomp.) 158.5—159 °C, R_f 0.15 (toluene—acetone, 20 : 1); $[\alpha]_D$ +149.4 (*c* 0.4, CH_2Cl_2). ^{31}P NMR, δ: 42.3 (br.s). ^{1}H NMR: signals of the palladacycle: 1.447 (s, 9 H, Bu^t); 2.993 (br.d, 3 H, NMe_{eq}, $^4J_{H,P}$ = 2.9 Hz); 3.242 (d, 1 H, α-CH, $^4J_{H,P}$ = 5.5 Hz); 2.615 (br.s, 3 H, NMe_{ax}); 5.856 (br.m, 1 H, H(6)); 6.210 (dt, 1 H, H(5), $^3J_{H,H}$ = 7.5 Hz, $^4J_{H,H}$ = 1.5 Hz); 6.728 (t, 1 H, H(4), $^3J_{H,H}$ = 7.4 Hz); signals of coordinated phosphine: 1.657 (d, 9 H, Bu^t, $^3J_{H,P}$ = 14.5 Hz); 2.421 and 2.849 (both s, 3 H each, Me); 7.615 (dd, 1 H, H_o, $J_{H,P}$ = 11.7 Hz, $^3J_{H,H}$ = 7.8 Hz); 6.8—7.42 (group of m, 8 H, H_o, 4H_m, 2H_p (**HL^{10}**), C(3)H (C_6H_4Pd)).

Chloro[(*R*,*S*)-2-{1-amino-2,2-dimethylpropyl}phenyl-*C*,*N*](*tert*-butyl-di-*o*-tolylphosphine-*P*)palladium(II) (*rac*-1h). A solution of dimer **1a** (28.6 mg, 0.0470 mmol) and phosphine **HL^{10}** (27.9 mg, 0.0987 mmol) in toluene (5 mL) was stirred at 20 °C for 19 h. The precipitate that formed was filtered off, washed with toluene, and dried *in vacuo*. Complex *rac*-**1h** was obtained as a colorless amorphous precipitate in a yield of 16.7 mg (31%). M.p. (with decomp.) 148—150 °C, R_f 0.25 (benzene—acetone, 10 : 1). Found (%): C, 60.97; H, 6.91; N, 2.47. $C_{29}H_{39}ClNPPd$. Calculated (%): C, 60.63; H, 6.84; N, 2.44. ^{31}P NMR, δ: 44.71 (br.s). ^{1}H NMR, δ: signals of the palladacycle: 1.32 (s, 9 H, α-Bu^t); 3.66 (br.d, 1 H, NH_{eq}, $^2J_{H,NH}$ = 11.1 Hz);

* The chemical shift of insoluble *PC*-dimer **10b** was determined from the spectrum of its mixture with adduct **10d** (1 : 1), which was generated *in situ* by the reaction of dimer **10b** with 1 equiv. of phosphine **HL^{10}**; the signals of adduct *trans*-**10d** (δ): 58.64 (d, $^2J_{P,P}$ = 373 Hz, *PC*-palladacycle) and 25.60 (d, $^2J_{P,P}$ = 373 Hz, coordinated phosphine **HL^{10}**).

* The complex partially decomposes on the sorbent to recover the starting dimer.

Table 2. Selected bond lengths and bond angles in the structure of complex (*S*)-**3c**

Bond	*d*/Å	Angle	ω/deg	Angle	ω/deg
Pd(1)—P(1)	2.3030(19)	C(1)—Pd(1)—N(1)	79.4(2)	C(7)—N(1)—C(12)	107.1(6)
Pd(1)—Cl(1)	2.413(2)	C(1)—Pd(1)—P(1)	99.5(2)	C(6)—C(1)—C(2)	117.1(5)
Pd(1)—C(1)	2.011(5)	N(1)—Pd(1)—P(1)	177.45(14)	C(6)—C(1)—Pd(1)	114.0(4)
Pd(1)—N(1)	2.154(5)	C(1)—Pd(1)—Cl(1)	167.77(17)	C(2)—C(1)—Pd(1)	128.2(5)
P(1)—C(21)	1.838(6)	N(1)—Pd(1)—Cl(1)	90.96(13)	C(5)—C(6)—C(1)	121.2(6)
P(1)—C(31)	1.855(5)	P(1)—Pd(1)—Cl(1)	90.39(5)	C(5)—C(6)—C(7)	120.5(6)
P(1)—C(41)	1.928(6)	C(21)—P(1)—Pd(1)	112.7(2)	C(1)—C(6)—C(7)	118.2(5)
N(1)—C(13)	1.475(9)	C(31)—P(1)—Pd(1)	119.01(17)	N(1)—C(7)—C(6)	104.4(5)
N(1)—C(7)	1.508(8)	C(41)—P(1)—Pd(1)	110.43(19)	N(1)—C(7)—C(8)	117.4(6)
N(1)—C(12)	1.515(9)	C(13)—N(1)—Pd(1)	117.8(5)	C(6)—C(7)—C(8)	114.4(6)
C(1)—C(6)	1.386(8)	C(7)—N(1)—Pd(1)	106.7(4)	N(1)—C(7)—H(7A)	111.0(4)
C(6)—C(7)	1.512(9)	C(12)—N(1)—Pd(1)	105.3(4)	C(6)—C(7)—H(7A)	115.0(4)
C(7)—C(8)	1.564(10)	C(21)—P(1)—C(31)	100.3(3)	C(9)—C(8)—C(7)	113.5(7)
C(7)—H(7A)	0.73(5)	C(21)—P(1)—C(41)	105.8(3)	C(10)—C(8)—C(7)	112.9(6)
C(8)—C(9)	1.533(10)	C(31)—P(1)—C(41)	107.5(3)	C(11)—C(8)—C(7)	108.2(7)
C(8)—C(10)	1.541(11)	C(13)—N(1)—C(7)	114.6(6)	C(21)—C(26)—C(27)	124.9(6)
C(8)—C(11)	1.522(13)	C(13)—N(1)—C(12)	104.5(6)	C(31)—C(36)—C(37)	124.1(6)

3.94 (dd, 1 H, α-CH, $^3J_{HC,NH_{ax}}$ = 6.5 Hz, $^4J_{H,P}$ = 6.1 Hz); 4.06 (br.dd, 1 H, NH_{ax}, $^2J_{H,NH}$ = 11.1 Hz, $^3J_{HN,CH}$ = 6.5 Hz); 5.92 (br.dd, 1 H, H(6), $^3J_{6,5}$ = 7.6 Hz, $J_{H,P}$ = 7.6 Hz; 6.30 (dd, 1 H, H(5), $^3J_{5,6}$ = 7.6 Hz, $^3J_{5,4}$ = 7.1 Hz); 6.76 (dd, 1 H, H(4), $^3J_{4,3}$ = 7.6 Hz, $^3J_{4,5}$ = 7.1 Hz); 6.88 (d, 1 H, H(3), $^3J_{3,4}$ = 7.6 Hz); signals of phosphine: 1.61 (d, 9 H, PBu^t, $^3J_{H,P}$ = 14.6 Hz); 2.38 and 2.66 (both s, 3 H each, Me); 7.00—7.45 (group of m, 5 H, 3 H_m, 2 H_p); 7.32 (m, 1 H, H_m); 7.81 and 8.32 (both br.m, 1 H each, H_o, $^3J_{H,P}$ = 8.6 Hz).

Bromo[(*R*,*S*)-2-{1-amino-2,2-dimethylpropyl}phenyl-*C*,*N*](*tert*-butyl-di-*o*-tolylphosphine-*P*)palladium(II) (*rac*-1j). A solution of dimer *rac*-**1b** (20.0 mg, 0.0287 mmol) and phosphine **HL**[10] (15.5 mg, 0.0574 mmol) in toluene (9 mL) was stirred at 20 °C for 6 h and concentrated. The precipitate that formed was filtered off, dried *in vacuo*, and purified by chromatography (*h* = 13 cm, *d* = 1.5 cm; $CHCl_3$ and a 40 : 1 $CHCl_3$—MeOH mixture as the eluents). Complex *rac*-**1b** was recrystallized from a diethyl ether—hexane mixture, and the precipitate was washed with hexane and dried *in vacuo*. Adduct *rac*-**1j** was obtained as a pale-yellow crystalline precipitate in a yield of 10.4 mg (29%). M.p. 213—215°, R_f 0.33 (chloroform—methanol, 20 : 1). Found (%): C, 56.40; H, 6.13; N, 2.16. $C_{29}H_{39}BrNPPd$. Calculated (%): C, 56.28; H, 6.35; N, 2.26. ^{31}P NMR, δ: 46.56 (br.s). ^{1}H NMR, δ, signals of the palladacycle: 1.31 (s, 9 H, α-Bu^t); 3.72 (br.d, 1 H, NH_{eq}, $^2J_{H,NH}$ = 9.4 Hz); 3.97 (dd, 1 H, α-CH, $^3J_{HC,NH}$ = 6.3 Hz, $^4J_{H,P}$ = 6.3 Hz); 4.04 (br.m, 1 H, NH_{ax}); 5.93 (br.dd, 1 H, H(6), $^3J_{6,5}$ = 8.5 Hz, $J_{H,P}$ = 4.4 Hz); 6.29 (dd, 1 H, H(5), $^3J_{5,6}$ = 8.5 Hz, $^3J_{5,4}$ = 6.9 Hz); 6.76 (dd, 1 H, H(4), $^3J_{4,5}$ = 6.9 Hz, $^3J_{4,3}$ = 7.5 Hz); 6.89 (d, 1 H, H(3), $^3J_{3,4}$ = 7.5 Hz); signals of coordinated phosphine: 1.62 (d, 9 H, Bu^t, $^3J_{H,P}$ = 15.1 Hz); 2.42 and 2.83 (both s, 3 H each, Me); 7.00—7.45 (group of m, 6 H, 4 H_m, 2 H_p); 7.49 and 8.27 (both br.m, 1 H each, H_o).

Spectroscopic determination of the enantiomeric purity of dimeric cyclopalladated complexes. *CN*-dimer 8a. A mixture of dimer **8a** (25.5 mg, 0.0362 mmol) and sodium (*S*)-prolinate (12.0 mg, 0.0875 mmol) in MeOH (5 mL) was stirred at 20 °C for 2 h and concentrated to dryness. The residue was dissolved in $CDCl_3$, and the ^{1}H NMR spectrum was measured. The spectrum reveals two sets of well-resolved signals identical to those described earlier[50] for diastereomers of (*S*)-prolinate adduct **8b**; their ratio was determined from the integral intensities of the signals for the α-CH protons.

***CS*-Dimer 11a**. A solution of (1*R*,2*R*)-1,2-diphenylethane-1,2-diamine (19.4 mg, 0.091 mmol) in MeOH (1 mL) was added to a suspension of dimer **11a** (31.0 mg, 0.0456 mmol) in MeOH (2 mL). The reaction mixture was stirred at 20 °C for 4 h and concentrated to dryness *in vacuo*. ^{1}H NMR spectrum of diamine adduct **11d** (δ) ($CDCl_3$: CD_3OD = 5 : 1; two sets of signals in a ratio of 1 : 1): signals of the palladacycle: 1.412 and 1.420 (both s, 9 H each, Bu^t); 1.45—2.20 (group of m, 19 H, 3β-H, 4β′-H, 4γ-H, $4NH_2$); 3.278 (m, 1 H, β-H_{eq}, $^2J_{H,H}$ = 13 Hz, $^3J_{\beta\text{-}H_{eq},\alpha\text{-}H_{ax}}$ = 2.6 Hz); 4.243 and 4.301 (both dt, 1 H each, α′-H_{ax}, $^2J_{H,H}$ = 13.0 Hz, $^3J_{\alpha\text{-}H_{ax},\beta\text{-}H_{ax}}$ = 10.1 Hz, $^3J_{\alpha\text{-}H_{ax},\beta\text{-}H_{eq}}$ = 2.9 Hz); 4.475 (br.d, 1 H, α′-H_{eq}, $^2J_{H,H}$ = 13 Hz); 4.734 and 4.779 (both dd, 1 H each, α-H_{ax}, $^3J_{\alpha\text{-}H_{ax},\beta\text{-}H_{ax}}$ = 12.3 Hz, $^3J_{\alpha\text{-}H_{ax},\beta\text{-}H_{eq}}$ = 2.6 Hz); signals of diamine:* 3.357 (m, 2 H, α-CH); 7.1—7.4 (m, 10 H, 2Ph).

***PC*-Dimers 9a and 10a,b**. A mixture of *PC*-dimer **9a** or **10a,b** (~0.030 mmol) and sodium (*S*)-prolinate (~0.063 mmol) in MeOH (5 mL) was stirred at 20 °C for 2 h and then concentrated to dryness. The residue was dissolved in $CDCl_3$, and the ^{31}P NMR spectrum of a mixture of diastereomers of (*S*)-prolinate derivatives **9b** or **10c** was measured. The spectroscopic parameters of adducts **9b** (see Ref. 40) or **10c** (see Ref. 41) are consistent with the characteristics published earlier.

X-ray diffraction study of compound **3c** was performed on an automated Enraf-Nonius CAD4 diffractometer (Mo-*K*α radiation, λ = 0.71073 Å) at room temperature. The experimental intensities were corrected for the Lorentz and polarization factors.[86] Absorption corrections were applied based on the intensities of equivalent reflections.[87] The structure was solved by direct methods (SHELXS-97).[88] All nonhydrogen atoms were

* The signals of the NH_2 groups of the diamine overlap with the signals of the piperidine ring.

Table 3. Crystallographic data and the X-ray data collection and refinement statistics for complex (*S*)-**3c**

Parameter	(*S*)-**3c**
Molecular formula	$C_{31}H_{43}ClNPPd$
Molecular weight	602.48
Crystal system	Orthorhombic
Space group	$P2_12_12_1$
a/Å	14.843(8)
b/Å	10.925(6)
c/Å	18.164(11)
V/Å^3	2945(3)
Z	4
d_{calc}/g cm^{-3}	1.359
μ/mm^{-1}	0.795
F(000)	1256
θ Scan range/deg	2.18—24.99
Ranges of indices of reflections	$-17 \le h \le 5$ $-2 \le k \le 12$ $-4 \le l \le 21$
Number of measured reflections	5786
Number of independent reflections (R_{int})	4436(0.0384)
Number of parameters in refinement	489
R_1 ($I \ge 2\sigma(I)$)	0.0323
wR_2 (based on all reflections)	0.0822
Goodness-of-fit on F^2	1.044
Flack parameter	−0.04(4)
Residual electron density (max/min)/e Å^{-3}	0.983/−0.916

refined by the full-matrix least-squares method against F^2 with anisotropic displacement parameters (SHELXL-97).[89] All hydrogen atoms were located in difference Fourier maps and refined isotropically. Selected bond lengths and bond angles are listed in Table 2. The crystallographic data and the X-ray data collection and refinement statistics for the structure of **3c** are given in Table 3.

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