Steric Promotion of Aromatic C–H Bond Activation in Primary Benzylamines

Valery V. Dunina,*[a] Lyudmila G. Kuz'mina,[b] Marina Yu. Kazakova,[a] Ol'ga N. Gorunova,[a] Yury K. Grishin,[a] and Elena I. Kazakova[c]

Keywords: Palladium / Primary benzylamines / NMR spectroscopy / Structure elucidation / Conformation analysis

ortho-Palladation of a sterically crowded primary benzylamine, α-phenylneopentylamine, was accomplished in a moderate yield of 50% in the reaction with the weakest of palladation agents (Li_2PdCl_4) under very mild conditions, due to a steric promotion of an aromatic C–H bond activation. The structure of dimer **1a** thus formed and the palladacycle conformation were established on the basis of ^{1}H-NMR spectroscopy of its mononuclear derivatives with [D_5]pyridine (**3a**) and triphenylphosphane (**4a**), and an X-ray investigation of the latter.

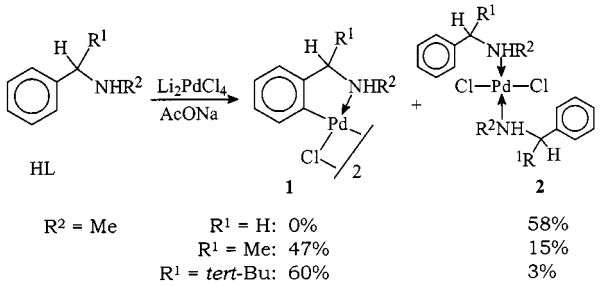
Introduction

Widening the scope of direct intramolecular palladation reactions is of great importance for further development of regioselective palladium-mediated organic synthesis.[1][2] In particular, cyclometallated derivatives of primary amines seem to be especially promising synthons for the heterocyclization processes based on a combined use of the C−Pd and N−H bond reactivities.[3−5] However, after initial unsuccessful attempts with the use of tetrachloropalladate,[6] the direct *ortho*-palladation reactions of these substrates proved to be elusive.

Several recent findings have made an important contribution towards a solution to this problem: (i) the use of palladation agents of higher electrophilicity; and (ii) the realization of the necessity for creating a coordination vacancy at a metal centre. The first point includes a substitution of palladium acetate for commonly used tetrachloropalladate salts.[7−11] The second goal may be simply achieved by keeping the palladium/ligand ratio equal to 1:1. It results in the formation of binuclear coordination complexes as reaction intermediates capable of dissociating easily to form two unsaturated tricoordinated species of high reactivity.[8][10] At this stage, a polar solvent may facilitate the dissociative formation of the coordination vacancy that is required for a subsequent C−H bond activation. In principle, all these problems may be solved simultaneously by utilizing the methodology involving a halide abstraction from the intermediate bis(amine) complexes [$Pd(HL)_2Hal_2$] by the action of soluble Ag^+ salts.[12][13]

Despite numerous publications dealing with the direct cyclopalladation of primary benzylamines, the possibility of steric promotion of this process still remains unexplored. The pioneer work of Lewis and co-workers[14] cannot be considered as conclusive enough because this publication does not contain any spectral evidence that the isolated (triphenylmethylamine)palladium complexes have a cyclopalladated structure.

Our investigation of the direct *ortho*-palladation of secondary arylalkylamines[15−19] has revealed a phenomenon of a remarkable steric facilitation of this process. The reaction of Li_2PdCl_4 with a series of *N*-methylbenzylamines was found to be dependent on the volume of substituent R^1 (R^1 = H, Me, *t*Bu) in the α-benzylic position.



Scheme 1. Steric promotion of aromatic C−H bond activation in secondary benzylamines

Thus, the reaction with α-nonsubstituted *N*-methylbenzylamine stops at the stage of the simple coordination complex of type **2**;[15] α-Me-substituted amine forms *ortho*-palladated dimer of type **1** only in refluxing methanol in moderate yield of 47%.[15] In contrast, α-*t*Bu-substituted analogue undergoes the cyclopalladation reactions even at room temperature in excellent yield of 86%.[18][20] Moreover, activation of sp^3 C−H bond (26%) becomes possible in the case of the latter sterically crowded benzylamine in competition with sp^2 C−H bond activation (60%) to give two possible regioisomers in a ca. 1:3 ratio.[20]

These findings gave an impetus for studying a similar steric effect in the C−H bond activation of primary benzylamines. The role of solvents, particularly acetone, in these processes is also of interest. Another task is the inves-

[a] Department of Chemistry, M. V. Lomonosov Moscow State University,
119899, V-234, Vrob′yovy Gory, Moscow, Russia
Fax: (internat.) + 7-095/932-8846
E-mail: dunina@org.chem.msu.su
[b] N. S. Kurnakov Institute of General and Inorganic Chemistry, Leninsky Prospect, 31, 117907, Moscow, Russia
[c] Department of Chemistry and Biology, Syktyvkar State University,
167005, Petrozavodskaya Street, 120, Syktyvkar, Komi Republik, Russia

Supporting information for this article is available on the WWW under http://www.wiley-vch.de/home/eurjic or from the author.

  1434−1948/99/0606−1029 $ 17.50+.50/0

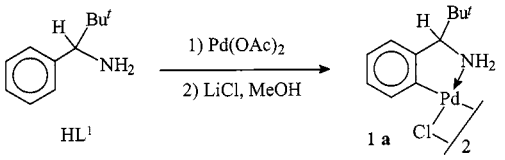
tigation of conformational features of the five-membered palladacycles containing a primary amino group using ^{1}H-NMR and X-ray studies. These characteristics seem to be especially important for utilization of the new kind of palladacycles in the processes of chiral recognition (for example, see ref.[21]).

Results and Discussion

Cyclopalladation Reactions

To estimate the role of steric effects in the processes of the intramolecular C−H bond activation in primary benzylamines, we have chosen α-phenylneopentylamine (HL^1) bearing a bulky *tert*-butyl group in the α-benzylic position as the most suitable ligand. In accordance with recent information regarding the cyclometalation mechanisms,[22−24] the equimolar ligand/Pd ratio was kept under all conditions to facilitate the formation of the free coordination vacancy after the first stage of the ligand-to-palladium *N*-coordination.

Firstly, a study of the HL^1 *ortho*-palladation was carried out using palladium(II) acetate, one of the most efficient reagents due to its high electrophilicity.



Conditions for 1) and yields: benzene, r.t., 24h - 43%
acetone, 50°C, 50h - 68%
MeOH, 50°C, 1.5 h - 68%
MeOH, r.t., 24h - 71%

Scheme 2. Influence of conditions on the *ortho*-palladation of the primary amine HL^1 with palladium(II) acetate

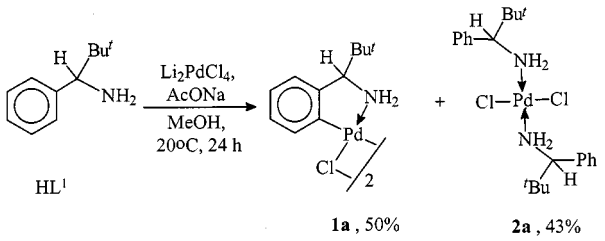
The reaction performed in benzene at room temperature afforded (after standard AcO^-/Cl^- metathesis and chromatographic purification) the desired dimeric chloro-bridged *ortho*-palladated complex **1a** in a 43% yield. In comparison, the α-methyl-substituted μ-bromo analogue was obtained previously under similar conditions in a yield of only 17% after one day, or in the same yield (43%) after three days.[9] Both enantiomers of the corresponding μ-chloro dimer were prepared by Fuchita in higher yields of 57−63% by means of a two-step procedure (including the isolation of the intermediate μ-acetato dimer) only after heating at 50°C for a long period of time.[11]

The yield of dimeric complex **1a** was increased to 68% by carrying out the same reaction in acetone at higher temperature (50°C); however, this procedure requires ca. 50 hours of heating. The best results were achieved when the reaction was performed in methanol; dimer **1a** was isolated in a yield of nearly 70% after heating for 1.5 hours at 50°C or after stirring for 24 hours at room temperature. In comparison, the formation of the α-Me-substituted analogue in a 50−70% yield required heating at 60°C for four hours.[21]

The results obtained in this series of *ortho*-palladation reactions with palladium(II) acetate make it evident that polar solvents have some advantages over the non-polar ones. It may be a consequence of their strong solvating effect that assists in the generation of the reactive three-coordinate intermediate of the [(HL)Pd(OAc)$_2$(Solv)]-type[8] required for subsequent C−H bond activation. Solvent basicity may also be important at the stage of C−H bond activation.[24]

The first successes in the palladation of primary benzylamines were achieved with the use of acetone as solvent.[8,11,13] Such a choice seems to be a rather strange one when the possibility of a metal-assisted interaction between the carbonyl and NH_2 groups is considered. Precedents for the C=N bond formation[25] and cleavage[26−28] at the palladium matrix are known. These transformations may allow the reaction to go through *ortho*-palladation of the more reactive short-lived ketimine intermediate. This route may result in the facilitation of the whole process. However, contrary to expectations, the use of acetone as solvent in the palladation of the amine HL^1 did not provide any advantages over the use of methanol; moreover, in this case, more vigorous conditions or increased reaction times are required. This observation allowed for the exclusion of the *ortho*-palladation route via intermediate ketimine ligand formation (at least for HL^1).

The results obtained when using the weak palladation agent Li_2PdCl_4 may be considered as the most convincing evidence for the steric promotion of the C−H bond activation: dimer **1a** was isolated in a 50% yield in the reaction performed in MeOH in the presence of sodium acetate excess at room temperature.



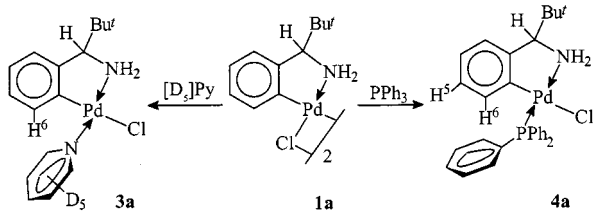
Scheme 3. *ortho*-Palladation of primary amine HL^1 using tetrachloropalladate

Under these conditions a simple coordination complex *trans*-[Pd(HL^1)$_2$Cl$_2$] (**2a**) was isolated in a yield of ca. 43% (based on the ligand) as a side product. Its 1:2 stoichiometry differs from the starting Pd/HL^1 ratio of 1:1 and may be explained by a partial Pd^{II} reduction. Under the same conditions, primary α-methylbenzylamine forms only a coordination compound of type **2**, which tends to decompose at increased temperatures.[15] The formation of complex **2a** occurs without any diastereoselectivity: a mixture of nearly equal amounts of (*R**,*R**)- and (*S*,*R*)-diastereomers was isolated in the reaction of racemic HL^1 with Li_2PdCl_4. One of these diastereomers may be separated by crystallization.

We believe that two main factors determine the easier *ortho*-palladation of the sterically hindered ligands (includ-

ing amine HL^1): (i) a large effective volume of the ligand must increase an internal energy of the intermediate binuclear coordination compounds due to a set of unfavourable non-bonding interactions,[29] thus stimulating an intermediate dissociation to form reactive three-coordinate species; (ii) the same steric effect must result in a weakening of the Pd−N bond in the coordination intermediate,[30] to make the palladium(II) centre more electrophilic. Both effects essentially facilitate the C−H bond activation.

For the subsequent spectral and structural investigations of the new dimeric complex **1a**, its mononuclear derivative with [D_5]pyridine (**3a**) was generated in situ, and an adduct with PPh_3 (**4a**) was prepared by a standard μ-chloro bridge cleavage.



Scheme 4. Mononuclear derivatives of the *ortho*-palladated primary amine HL^1

The identity of the samples of dimer **1a** prepared under all afore-mentioned conditions was confirmed by their melting points, TLC of complex **1a** and the ^{1}H-NMR spectra of its mononuclear derivatives **3a** and **4a**.

Structure of Complexes 1a−4a in Solution

The *ortho*-palladated structure of complexes **1a**, **3a** and **4a** was confirmed by the IR and ^{1}H-NMR spectra (Table 1) using a comparison with the spectral data for simple coordination compound **2a**. An assignment of their ^{1}H-NMR spectra was based on homonuclear spin-spin decoupling experiments and NOE differential spectroscopy.[31]

The IR spectrum of dimer **1a** contains a single intense absorption of the aromatic C−H bonds out-of-plane deformation at 740 cm^{-1}[18,19,32,33] compared to two bands found in the IR spectra of the free starting amine HL^1 and coordination complex **2a** (720, 785 and 705, 750 cm^{-1}, respectively). The ^{1}H-NMR spectra of mononuclear adducts **3a** and **4a** reveal only four well-resolved single-proton resonances of the *ortho*-phenylene group in the aromatic field (δ = 6.0−7.0), compared to two complicated multiplets of *ortho* (δ = 7.00, 4 H) and *meta* and *para* protons (δ = 7.27, 6 H) further downfield in the case of coordination complex **2a**.

The nine-proton singlet of the *t*Bu group (δ = 1.23−1.30 for adducts **3a** and **4a**) unambiguously supports the suggestion that the palladation site is the *ortho*-position of benzylamine Ph ring. Both the diastereotopic nonequivalence (Δδ = 0.3−2.7 ppm) and the coordination shift values (Δδ = 1.7−4.5 ppm) observed for the two NH_2 protons in the complexes **2a**−**4a** confirm the *Pd*-coordination of the primary amino group. Thus, the η^1-*N*-coordination of the HL^1 ligand in complex **2a** and η^2-*C*,*N*-binding of the $(L^1)^-$ ligand in adducts **3a**, **4a** and also in starting dimer **1a** are evident enough.

The assignment of the signals of the aromatic palladacycle protons is important not only for the confirmation of the *ortho*-palladated structure and the geometric configuration of these and related complexes, but also for the utilization of the palladacycle as an internal reference in the estimation of the stereochemistry of *Pd*-bonded chiral ligands.[34−39]

Unfortunately, most publications devoted to the *ortho*-palladation of primary benzylamines either disregard any

Table 1. ^{1}H-NMR-spectroscopic data for ligand HL^1 and its palladium complexes **2**−**4**[a]

	Side chain protons				Aromatic protons [b]			
	tBu, 9 H	α-C*H*, 1 H	N*H*^{1}, 1 H	N*H*^{2}, 1 H	*H*^{6}, 1 H	*H*^{5}, 1 H	*H*^{4}, 1 H	*H*^{3}, 1 H
HL^1	0.91 (s)	3.69 (s)	1.40 (br. s., 2 H)		7.21−7.32 (m, 5 H)			
2a[c]	0.83 (s)	3.73 (dd, $^3J_{HCNH^1}$ = 11.2, $^3J_{HCNH^2}$ = 3.1)	3.11 (br. tr, $^2J_{HNH}$ = 11.0, $^3J_{HNCH}$ = 11.2)	3.81 (br. d, $^2J_{HNH}$ = 11.0, $^3J_{HNCH}$ = 3.1)	7.00 (m, 2 H, *ortho*-H), 7.27 (m, 3 H, *meta*- and *para*-H)			
3a	1.23 (s)	3.96 (d, $^3J_{HCNH}$ = 5.7)	3.16 (br. d, $^2J_{HNH}$ = 10.7)	5.89 (br. m, $^3J_{HCNH}$ = 5.7, $^2J_{HNH}$ = 10.7)	6.04 (A-part, $^3J_{5,6}$ = 7.7, $^4J_{4,6}$ = 1.2)	6.75 (B-part, $^3J_{4,5}$ = 7.4, $^4J_{3,5}$ = 1.4)	6.98 (C-part, $^3J_{3,4}$ = 7.6, $^4J_{4,6}$ = 1.2)	7.01 (D-part, $^3J_{3,4}$ = 7.6, $^4J_{3,5}$ = 1.4)
4a[d]	1.30 (s)	4.06 (dd, $^3J_{HCNH}$ = 5.8, $^4J_{HP}$ = 6.5)	3.73 (br. dd, $^2J_{HNH}$ = 10.6, $^3J_{HNP}$ = 3.1)	4.01 (br. m, $^2J_{HNH}$ = 10.6, $^3J_{HNCH}$ = 5.8, $^3J_{HNP}$ = 5.0)	6.39 (A-part, $^3J_{5,6}$ = 7.7, $^4J_{4,6}$ = 1.3, J_{HP} = 6.0	6.44 (B-part, $^3J_{4,5}$ = 7.4, $^4J_{3,5}$ = 1.5, J_{HP} = 0.5)	6.83 (C-part, $^3J_{3,4}$ = 7.4, $^4J_{3,5}$ = 1.3)	7.00 (D-part, $^3J_{3,4}$ = 7.7, $^4J_{3,5}$ = 1.5)
4a[e,f]	1.28 (s)	4.07 (dd, $^3J_{HCNH}$ = 6.0, $^4J_{HP}$ = 7.0)	3.58 (br. d, $^2J_{HNH}$ = 10.6, $^3J_{HNP} \leq$ 1.0)	5.18 (br. m, $^2J_{HNH}$ = 10.6, $^3J_{HNCH}$ = 6.0, $^3J_{HNP}$ = 4.0)	6.31 (m, 2 H, H^5 + H^6)		6.78 (m)	6.95 (m)

[a] Spectra recorded at 400 MHz in $CDCl_3$ (except where noted), δ in ppm relative to TMS as internal standard, *J* in Hz. − [b] ABCD system in the case of **3a**, ABCDX system (X = ^{31}P) for **4a**. − [c] Spectrum of individual (*R*,*R*)* diastereomer. − [d] Signals of PPh_3 protons ($CDCl_3$): δ = 7.36 (m, 6 H, *meta*-H), 7.42 (m, 3 H, *para*-H), 7.73 (m, 6 H, $^3J_{HP}$ 11.1, *ortho*-H). − [e] Spectrum was recorded in [D_6]acetone/$CDCl_3$, 10:1. − [f] Signals of PPh_3 protons: δ = 7.35 (m, 6 H, *meta*-H), 7.42 (m, 3 H, *para*-H), 7.70 (m, 6 H, $^3J_{HP}$ 11.2, *ortho*-H), 1.95 (s, 3 H, MeCN).

assignments of the aromatic protons[9,13,21] or do so only in part.[11] Moreover, several attempts to assign these signals for phosphane adducts[8][10] gave a result which strongly disagreed with the usual trends reported for the related derivatives of secondary[7,18,19,40,41] and tertiary [33,42−44] benzylamines. This disagreement includes three points: (i) the most downfield signal was assigned to the H^6 proton (nearest to the metallation site); (ii) as a result, the long-range constant $^5J_{HP}$ of a very high value was ascribed to the H^3 proton that is far remote from the ^{31}P nucleus; (iii) at the same time, the corresponding constant for the H^6 proton is lacking despite its proximity to the ^{31}P nucleus being closer than the sum of their van der Waals radii of 3.0 Å[45] (for example, 2.78 Å was found by the X-ray study of a related complex[46]).

Such a large discrepancy between the spectral characteristics of palladacycles for derivatives of primary benzylamines on the one hand, and those of secondary and tertiary amines on the other, forced us to provide unambiguous support for our version of assignment on the basis of the NOE differential spectra of the phosphane adduct **4a**.

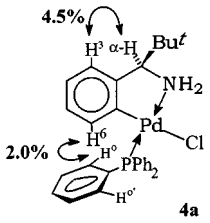


Figure 1. Selected $^1H\{^1H\}$ NOEs for the phosphane adduct **4a** in $CDCl_3$

The irradiation of the low-field H^3 proton of the palladated phenylene ring (δ = 7.00 for the **4a** in $CDCl_3$) results in an enhancement of ca. 4.5% of the signal for the α-benzylic methine proton nearest to H^3 (see Figure 1); when the *ortho*-protons of the PPh groups were irradiated (δ = 7.73, identified on the basis of the constant value of $^3J_{HP}$ = 11.1 Hz) the only observed interligand response was that of the H^6 proton (δ = 6.39, ca. 2%). Hence, a downfield position of the H^3 signal and an upfield location of the H^6 resonance of the palladated phenylene group are evident.

Thus, in the ^1H-NMR spectra of the arylphosphane adducts of *ortho*-palladated primary benzylamines, the sequence of the signals of the phenylene H^6-H^3 protons remains the same as in the case of their analogues derived from secondary and tertiary amines, namely, from high field (H^6) to low field (H^3). This tendency, as well as the detection of the J_{HP} constant for the H^6 proton, may be used for the reliable estimation of the geometric configuration and for the solution of stereochemical problems by means of NOE technique (cf. ref.[39,47,48]) using palladacycles as an internal reference.

A *trans*(C,Cl) geometry of the mononuclear derivatives of dimer **1a** seems to be evident enough from the high field position of the signals of the H^6 proton (**3a**) or the H^6 and H^5 protons (**4a**) of the palladated phenylene moiety, caused by the influence of anisotropy of the pyridine or *P*-phenyl rings, respectively. The large high-field value of the H^6 resonance in the ^1H-NMR spectrum of adduct **3a** (δ = 6.04) may be considered as an indication of the nearly orthogonal mutual arrangement of the pyridine and palladated phenylene rings.[49]

In the case of phosphane derivative **4a**, the signal of the H^6 proton appears at δ = 6.39, with the constant J_{HP} = 6.0 Hz, which is in close agreement with the values previously reported for related derivatives of primary aralkylamines (J_{HP} = 5.5−6.4 Hz).[50][51] For the more distant aromatic H^5 proton, this value decreases to J_{HP} = 0.5 Hz; it can only be detected by means of an NMR-spectrum simulation.

The conformation of the palladacycle formed by primary benzylamine HL^1 could be estimated by means of the analysis of the $HC^{\alpha}-NH$, $HC^{\alpha}-^{31}P$ and $HN-^{31}P$ spin-spin coupling constants. A strong dependence of the efficiency of the interaction between the protons of palladacycle and the ^{31}P nucleus of *Pd*-bonded phosphane ligands on the extent of their planarity may be expected from general considerations.[52][53]

A distinction in the assignments of two NH protons (NH^{eq} and NH^{ax}) is not a simple problem. In most reported ^1H-NMR spectra of *ortho*-palladated primary aralkylamines, these resonances were described as broad multiplets[8,13,21,51] or broad singlets[9][11] without their assignments. In the spectrum of pyridine adduct **3a** recorded in $CDCl_3$, the diastereotopic NH_2 proton signals appear as a broad apparent singlet (Δν > 20 Hz) and a broad doublet at δ = 5.89 and 3.14, respectively, with a typical geminal coupling constant of $^2J_{NH\text{-}NH} \approx 11$ Hz (cf. ref.[51,54,55]).

Homonuclear decoupling of adduct **3a** showed that a broad downfield signal at δ = 5.89 originates from the NH proton interacting with the α-methine proton ($^3J_{HCNH}$ = 5.7 Hz). In the case of phosphane adduct **4a**, the signals of NH protons are additionally complicated due to their spin-spin coupling with the ^{31}P nucleus. In the ^1H-NMR spectrum of **4a** measured in a $[D_6]$acetone/$CDCl_3$ mixture, two NH proton signals appear as a broad multiplet at δ = 5.19 ($^3J_{HNP}$ = 4.0 Hz, $^3J_{HCNH}$ = 6.0 Hz) and a doublet at δ = 3.58 ($^3J_{HNP} \leq 1.0$ Hz) with a geminal coupling constant of $^2J_{HNH}$ = 10.6 Hz.

Under these conditions, the α-methine proton of **4a** appears as a doublet of doublets at δ = 4.13 with the $^3J_{HCNH}$ and $^4J_{HCP}$ constants of 6.0 and 7.0 Hz, respectively. Both of these constants seem to be extremely useful for conformational analysis. The dependence of ^1H-^{31}P spin-spin coupling on the position of the α-CH proton (*pseudo*-axial or *pseudo*-equatorial) becomes evident from the spectral pattern for α-nonsubstituted palladacycles. Only one of the diastereotopic protons of the α-CH_2 group in phosphane adducts of *ortho*-palladated secondary[7][19] and tertiary benzylamines[56] shows a coupling with the ^{31}P nucleus ($^4J_{HCP}$ = 2.0−4.2). The average constant value of $^4J_{HCP}$ = 2.8 Hz reported for the two equivalent (on NMR time scale) α-benzylic protons in the more flexible α,*N*-nonsubstituted palladacycles,[50] may be used as a middle point for the conformation estimates. The $^4J_{HCP}$ = 6−8 Hz reported

for the strictly planar aldimine palladacycles may serve as the upper boundary point.[21][57]

The values of the $^4J_{HCP}$ constant for the α-methine proton ranging within 6.5−7.0 Hz in the ^{1}H-NMR spectra of complex **4a** are close to the above-mentioned upper limit. It may serve as an indication of its *pseudo*-equatorial position which is in agreement with the prediction of a *pseudo*-axial position of a bulky α-*t*Bu group. A comparison of these characteristics with those for the related derivatives of secondary[18][41] and tertiary α-*tert*-butylbenzylamines[44] ($^4J_{HCP}$ = 5.4−6.1 Hz) allows for a suggestion that a steric interaction between the α-*t*Bu substituent and the aromatic H^3 proton is the main factor controlling the palladacycle conformation. The role of the *N*-substituents seems not to be very significant in this case, in contrast with the assumption made previously.[58][59]

Unfortunately, no information could be found regarding the $^4J_{HCP}$ constant for the α-methine proton of related α-Me-substituted palladacycles based on primary arylalkylamines; usually this signal was described as a multiplet,[8][13] or a broad multiplet.[9][21] If the signal of the α-methine proton for the *ortho*-palladated derivative of primary α-(1-naphthyl)ethylamine is really a pure quadruplet as was reported,[51] the value of this constant must be equal to zero. Hence, the palladacycle must adopt the conformation with the α-Me group in an equatorial position, which contradicts the data ($^4J_{HCP}$ = 5.8-6.3 Hz) reported for related derivatives of the corresponding tertiary amine containing η^1-*P*-bonded phosphane ligands.[60−63]

A valuable additional source of stereochemical information is the HN−C^{α}H coupling. Newman projections along the N−C^{α}H bond for two possible conformations of the palladacycle, λ(*S*) and δ(*S*) (Figure 2), were constructed with regard to the real values of the torsion angles taken from the X-ray study of adduct **4a** (see the next section).

λ(*S*) δ(*S*)

Figure 2. Newman projections of (*S*)-palladacycle along the N−C(α) bond for two possible conformations, λ(*S*) and δ(*S*)

The most important dihedral angles between the C^α−H and the *pseudo*-axial and *pseudo*-equatorial N−H bonds for the λ(*S*) conformation are equal to ca. 31° and −88°, respectively, in the crystal of **4a**. As a result, an observable $^3J_{HCNH}$ constant can be predicted only for one of the two NH protons, namely NH^{ax}, if the same λ(*S*) conformation remains in solution. This particular situation takes place in the case of adducts **3a** and **4a**: $^3J_{HCNH}$ = 5.6−6.0 Hz was found for only one downfield resonance of the NH proton.

In contrast, in the case of the hypothetical δ(*S*) conformation of the palladacycle, the dihedral angles between the C^α−H and axial and equatorial N−H bonds should be nearly equal to one another from the point of view of the Carplus−Conroy equation[64] (ca. −30° and −150°, respectively). Hence, nearly equal values of the $^3J_{HCNH}$ constant are expected for both of the NH protons of the primary amino group. Moreover, the C^α−H bond in this conformation should be oriented nearly orthogonally to the mean coordination plane, and the $^4J_{HCP}$ constant for this proton should be approximately zero (cf. ref.[52,53,65]).

All these arguments allow for the exclusion of the δ(*S*) conformation of palladacycle in **3a** and **4a** from the consideration. It should be noted that the opposite (and incorrect) conclusion can be made from the analysis of "classic" Newman projections constructed without regard for the palladacycle flattening (with all dihedral angles equal to 60°): nearly equal $^3J_{HCNH}$ constant values have to be predicted for both NH protons in the λ(*S*) conformation and different values only for the δ(*S*) skew-envelope. The difference in the predicted values of the $^3J_{HCNH}$ constant may serve as a basis of the reliable criteria for identification of the axial and equatorial NH protons in the palladacycles derived from primary and secondary benzylamines.

As additional support for the axial position of the *t*Bu group in the palladacycle of λ(*S*) or δ(*R*) conformation, the downfield shift of its signal compared to the free ligand HL^1 should be mentioned (Δδ = 0.4−0.5 ppm for the complexes **3a** and **4a**). Commonly, such an effect is considered as a consequence of the metal anisotropy influence.[66][67] In the case of **3a** and **4a** complexes, the actual shift calculated for one proton must be essentially higher (Δδ up to 4 ppm) if one keeps in mind that each of the nine protons of the *t*Bu group spends nearly one ninth of all time in the proximity to the metal centre. Such a high shift may serve as an indirect indication for a weak *t*Bu···Pd agostic interaction.[66−69]

All these data support our statement that the palladacycles of dimer **1a** and its mononuclear derivatives **3a** and **4a** exist in solutions predominantly in the λ(*S*) or δ(*R*) conformation with the equatorial α-CH proton and the axial *t*Bu group. This result is important for further practical use of this new chiral matrix, because the conformational rigidity of palladacycles enhances their ability for chiral recognition.[36,52,53,63,70,71]

The relation between the $^3J_{HNP}$ constants for the two N−H protons of the primary amino group is difficult to predict. Taking into account the similar dihedral angles H^{ax}−N−Pd−P and H^{eq}−N−Pd−P, found for adduct **4a** in the crystal (110.7° and −130.9°, respectively), it is conceivable to suggest that both NH protons may reveal a spin-spin coupling with the ^{31}P nucleus. A little more efficient interaction may be expected for the *pseudo*-equatorial NH proton. However, the ^{1}H-NMR spectrum of **4a** reveals the reverse relation, namely, $^3J_{HNP}$ = 4.0−5.0 and 1.0−3.1 Hz for the NH^{ax} and NH^{eq} protons, respectively. Examples of equal[37,38,62,72] and substantially different[36,60,62,73] values of the $^4J_{HP}$ constant for NMe groups may be found among the spectra of phosphane complexes with the *ortho*-palladated *N*,*N*-dimethyl-α-(1-naphthyl)ethylamine, despite a high conformational stability of this palladacycle. This ob-

servation made the J_{HP} values for NH_2 and NMe_2 groups less suitable for the conformation analysis.

The structure of coordination complex **2a** can shed some light on the nature of the steric promotion of *ortho*-palladation reactions. Its ^{1}H-NMR spectrum indicates a restricted rotameric mobility of η^1-*N*-coordinated ligand HL[1]. A large difference between $^3J_{HCNH}$ constant values for two NH protons (11.2 and 3.1 Hz) pointed to the φ^3 or φ^5 conformation of *Pd*-bonded amine, with *transoid* orientation of one of the NH protons relative to the α-methine one. For the alternative φ^1 rotamer, nearly equal and low values of $^3J_{HCNH}$ constant may be predicted[64] from the Newman projections (Figure 3).

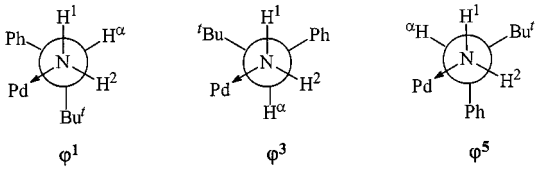


Figure 3. Newman projections of *Pd*-coordinated (*S*)-α-phenylneopentylamine along the N−C(α) bond for three main rotamers, φ^1, φ^3 and φ^5

The absence of deshielding effects (caused by the metal anisotropy[66−69]) for the *t*Bu protons in the spectra of complex **2a** (δ = 0.83 is close to δ = 0.91 for the free ligand HL[1]) allows for the differentiation between φ^3 and φ^5 rotameric forms in favour of the latter, where the *t*Bu group is far remote from the palladium centre.

Therefore, at the stage of monodentate *N*-coordination, the bulky HL[1] ligand adopts predominantly the φ^5 conformation with the Ph ring disposed in proximity to the metal centre (cf. ref.[74][75]). This conformation seems to be the most suitable starting state for the subsequent *ortho*-palladation. In contrast, monodentate *N*-coordination of the related α-Me-substituted primary benzylamine in the framework of binuclear μ-acetato coordination complex occurs in the φ^3 conformation with remote *transoid* position of the Ph ring with respect to the palladium centre.[10] Such a difference in the starting rotameric states of *N*-coordinated α-*t*Bu- and α-Me-substituted primary benzylamines may contribute to some extent to the steric promotion of the C−H bond activation in the former instance.

X-ray Structure Investigation of Phosphane Derivative 4a

Suitable crystals of triphenylphosphane adduct **4a** were grown from a dichloromethane/acetonitrile mixture. The molecular structure of the complex is presented in Figures 4 and 5; selected bond lengths and angles are given in Tables 2 and 3, respectively.

Only two other triphenylphosphane adducts of *ortho*-palladated primary benzylamines have been previously characterized structurally, namely, that of the α-Me-substituted analogue (*R*)-**4b**[13] and of the 2-phenylglycine methyl ester derivative (*R*)-**4c**.[11] The related derivative of 2-phenylethylamine containing a six-membered palladacycle was also studied by X-ray diffraction.[10]

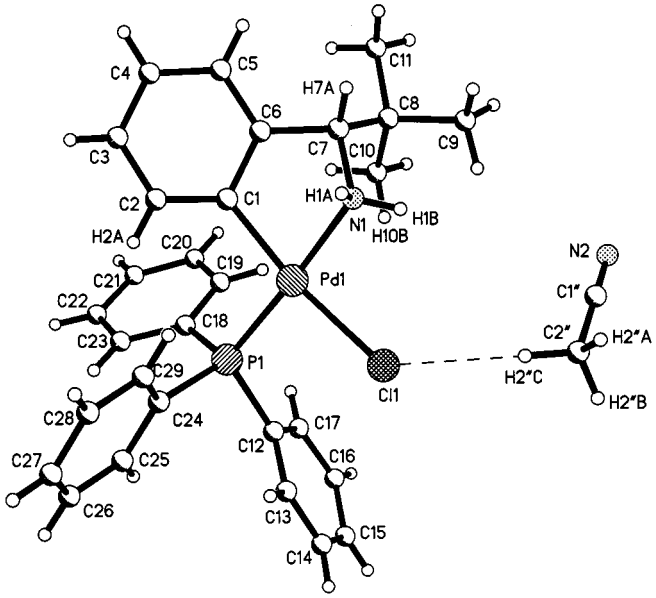


Figure 4. Molecular structure of the acetonitrile solvate of phosphane adduct **4a**

Table 2. Bond lengths [Å] for [2-(1-amino-2,2-dimethylpropyl)phenyl-*C*,*N*]chloro(triphenylphosphane)palladium(II)·MeCN solvate **4a**

Pd(1)−C(1)	2.006(4)	C(12)−C(13)	1.381(6)
Pd(1)−N(1)	2.087(4)	C(13)−C(14)	1.379(7)
Pd(1)−P(1)	2.256(2)	C(14)−C(15)	1.356(8)
Pd(1)−Cl(1)	2.3996(14)	C(15)−C(16)	1.370(8)
P(1)−C(24)	1.817(5)	C(16)−C(17)	1.382(8)
P(1)−C(12)	1.827(4)	C(18)−C(19)	1.383(6)
P(1)−C(18)	1.826(5)	C(18)−C(23)	1.391(6)
N(1)−C(7)	1.496(5)	C(19)−C(20)	1.376(7)
C(1)−C(2)	1.385(6)	C(20)−C(21)	1.365(9)
C(1)−C(6)	1.423(6)	C(21)−C(22)	1.372(9)
C(2)−C(3)	1.395(6)	C(22)−C(23)	1.403(8)
C(3)−C(4)	1.369(7)	C(24)−C(29)	1.379(6)
C(4)−C(5)	1.384(7)	C(24)−C(25)	1.390(6)
C(5)−C(6)	1.387(6)	C(25)−C(26)	1.376(7)
C(6)−C(7)	1.510(6)	C(26)−C(27)	1.371(8)
C(7)−C(8)	1.544(6)	C(27)−C(28)	1.374(8)
C(8)−C(11)	1.526(7)	C(28)−C(29)	1.390(7)
C(8)−C(10)	1.531(7)	N(2)−C(1″)	1.129(11)
C(8)−C(9)	1.537(7)	C(1″)−C(2″)	1.448(11)
C(12)−C(17)	1.377(7)		

Complex **4a** exists in the crystal as a racemate; the unit cell contains two centrosymmetrically related enantiomers of the mononuclear complex and two solvate molecules of acetonitrile (Figure 4). *ortho*-Palladated structure of adduct

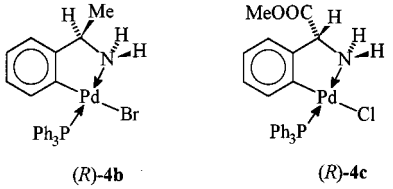


Table 3. Bond angles [°] for [2-(1-amino-2,2-dimethylpropyl)phenyl-*C*,*N*]chloro(triphenylphosphane)palladium(II)·MeCN solvate **4a**

C(1)−Pd(1)−N(1)	80.6(2)	C(11)−C(8)−C(7)	109.0(4)
C(1)−Pd(1)−P(1)	96.00(13)	C(10)−C(8)−C(7)	112.0(4)
N(1)−Pd(1)−P(1)	176.38(11)	C(9)−C(8)−C(7)	109.4(4)
C(1)−Pd(1)−Cl(1)	169.37(12)	C(17)−C(12)−C(13)	117.4(4)
N(1)−Pd(1)−Cl(1)	89.04(11)	C(17)−C(12)−P(1)	122.2(4)
P(1)−Pd(1)−Cl(1)	94.39(5)	C(13)−C(12)−P(1)	120.4(3)
C(24)−P(1)−C(12)	103.4(2)	C(14)−C(13)−C(12)	121.4(5)
C(24)−P(1)−C(18)	107.2(2)	C(15)−C(14)−C(13)	120.2(5)
C(12)−P(1)−C(18)	103.0(2)	C(14)−C(15)−C(16)	119.7(5)
C(24)−P(1)−Pd(1)	111.8(2)	C(15)−C(16)−C(17)	120.0(6)
C(12)−P(1)−Pd(1)	115.42(14)	C(16)−C(17)−C(12)	121.2(5)
C(18)−P(1)−Pd(1)	114.9(2)	C(19)−C(18)−C(23)	118.6(4)
C(7)−N(1)−Pd(1)	110.5(3)	C(19)−C(18)−P(1)	118.3(3)
C(2)−C(1)−C(6)	117.1(4)	C(23)−C(18)−P(1)	123.1(4)
C(2)−C(1)−Pd(1)	129.7(3)	C(20)−C(19)−C(18)	121.9(5)
C(6)−C(1)−Pd(1)	112.9(3)	C(21)−C(20)−C(19)	119.4(6)
C(1)−C(2)−C(3)	122.3(4)	C(22)−C(21)−C(20)	120.4(5)
C(4)−C(3)−C(2)	119.9(5)	C(21)−C(22)−C(23)	120.6(5)
C(3)−C(4)−C(5)	119.5(5)	C(18)−C(23)−C(22)	119.0(5)
C(4)−C(5)−C(6)	121.4(4)	C(29)−C(24)−C(25)	118.6(4)
C(5)−C(6)−C(1)	119.8(4)	C(29)−C(24)−P(1)	119.5(4)
C(5)−C(6)−C(7)	121.9(4)	C(25)−C(24)−P(1)	121.7(4)
C(1)−C(6)−C(7)	118.2(4)	C(26)−C(25)−C(24)	121.0(5)
N(1)−C(7)−C(6)	105.1(3)	C(27)−C(26)−C(25)	120.0(5)
N(1)−C(7)−C(8)	112.3(4)	C(26)−C(27)−C(28)	119.8(5)
C(6)−C(7)−C(8)	117.0(4)	C(27)−C(28)−C(29)	120.5(5)
C(11)−C(8)−C(10)	108.6(5)	C(24)−C(29)−C(28)	120.0(5)
C(11)−C(8)−C(9)	107.9(5)	N(2)−C(1″)−C(2″)	178.3(11)
C(10)−C(8)−C(9)	109.8(5)		

4a (and, therefore, that of starting dimer **1a**) is supported. The complex has a *trans*(C,Cl) geometry, expected from the spectral data. The Pd−C and Pd−N bond lengths [2.006(4) and 2.087(4) Å, respectively] are similar to those reported for other derivatives of primary benzylamines (2.019 and 2.092−2.089 Å for **4b** and **4c**, respectively).[10,11,13] The shorter value of the Pd−N bond in the structures of complexes **4a−c**, compared to that reported for the related derivatives of tertiary benzylamines [for example, 2.19(1) Å for *N*-isopropyl-*N*,α-dimethylbenzylamine analogue[46]] may serve as reliable evidence in favour of a tighter coordination of the primary amino group with the palladium centre.

The palladium atom in complexes **4a** and **4b** has nearly square-planar coordination with a slight tetrahedral distortion: the dihedral angles between the planes (CPdN) and (PPdHal) fall within the range 2.7−7.8°.

The palladacycle conformation in adduct **4a** may be described as a distorted envelope with the nitrogen atom displaced from the plane ($PdC^1C^6C^7$) of the remaining four atoms by −0.5999 Å as compared to −0.5113 and 0.399 Å for **4b** and **4c**, respectively. As a measure of a palladacycle twisting, the value of the dihedral angle between the phenylene ring of the benzylaminate ligand (C_6H_4) and the mean coordination plane (PdC^1HalNP) may be used. The values equal to 20.0 and 15.5° for **4a** and **4b**, respectively, indicate a more puckered conformation of the α-*t*Bu-substituted palladacycle.

The stereochemistry of palladacycle conformation is in agreement with the ^{1}H-NMR data in solutions, namely, λ for the (*S*), and δ for the (*R*) enantiomer. The bulky α-*t*Bu substituent assumes a position close to the axial one and the α-methine proton is arranged nearly equatorially: C^7-C^8 and C^7-H^{7a} bonds form angles of 168.4° (an adjacent angle 11.6°) and 66.9°, respectively, with the normal to the mean coordination plane.

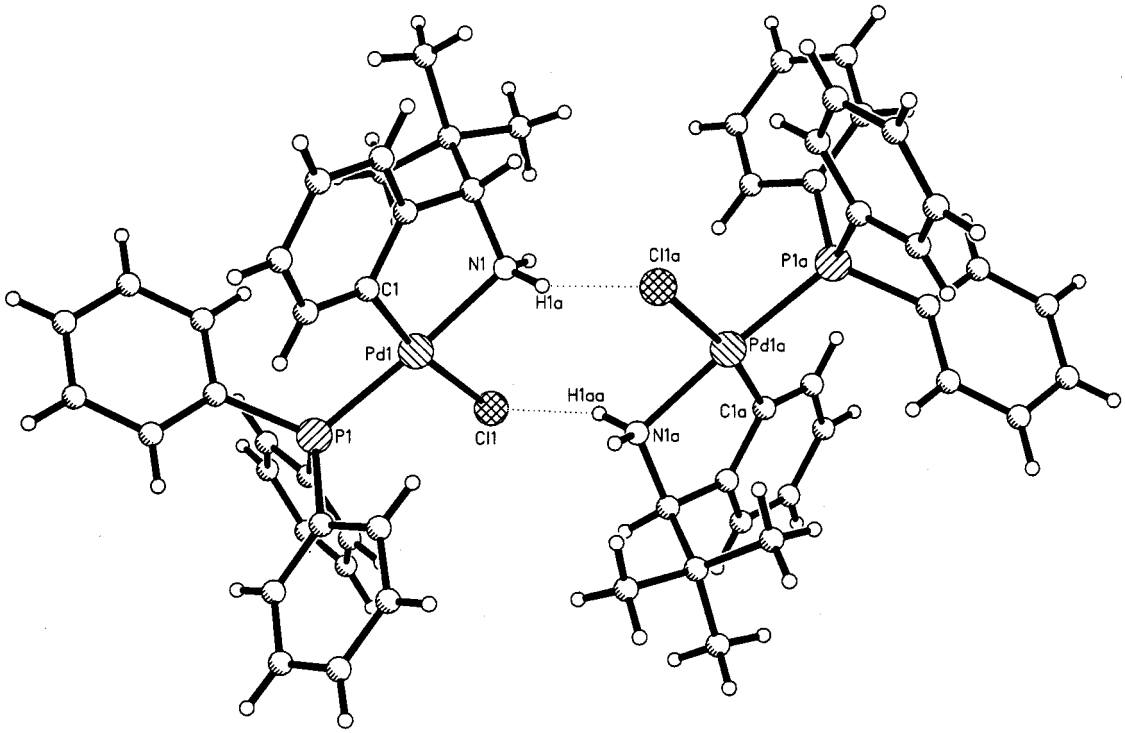


Figure 5. The mutual arrangement of two H-bonded (N−H···Cl) centrosymmetrically related enantiomers of phosphane adduct **4a** in the crystal

It is probable that a weak agostic interaction between one of the Me groups of the *t*Bu substituent with the palladium centre contributes to some extent to a stabilization of this conformation: the $H^{10b}\cdots Pd$ distance is 2.802 Å, which is less than the sum of the van der Waals radii for these atoms (3.1 Å[45]). It is noteworthy that similar secondary interactions were previously observed in the structures of *ortho*-palladated derivatives of α-*tert*-butyl-*N*,*N*-dimethylbenzylamine, namely, of a dimer (2.91−2.92 Å[76]) and its mononuclear derivative with pyridine (2.74−2.85 Å[20]).

The presence of the primary amino group in the palladacycle of **4a** results in a specific packing of molecules in the crystal, based on the hydrogen bonds of the type N−H···Cl (see Figure 5). Two enantiomers of the racemic complex are bonded in a centrosymmetric dimer by means of two rather strong hydrogen bonds, with the $NH^{1a}\cdots Cl^{1a}$ distances being equal to 2.416 Å, which is essentially less than the sum of the van der Waals radii for these atoms (3.3 Å[45]). The similar NH···Br hydrogen bonds (2.46 Å) were also found in the structure of α-Me-substituted analogue **4b**.[13]

In the crystal, the solvate acetonitrile is bonded with the coordinated chlorine atom by means of a hydrogen bond involving a methyl hydrogen atom (see Figure 4): The $CH^{2''f}\cdots Cl^{1}$ distance of 2.672 Å is also less than the sum of the van der Waals radii for these atoms (3.3 Å[45]).

Conclusions

The possibility of a steric promotion of the aromatic C−H bond activation in primary benzylamines bearing only one bulky α-substituent was shown. *ortho*-Palladation of α-phenylneopentylamine may be achieved under very mild conditions, using Li_2PdCl_4 in methanol at room temperature.

To the best of our knowledge, this work is the first presentation of the completely interpreted ^{1}H-NMR spectra of *ortho*-palladated primary benzylamine. It allows for establishing that the palladacycle formed adopts the λ(*S*) or δ(*R*) conformation with an axially oriented α-*t*Bu group both in the crystal and in solution. It seems reasonable to propose that such stereochemistry is dictated by unfavourable interactions between a bulky equatorial α-substituent and the neighbouring phenylene proton in alternative δ(*S*) or λ(*R*) conformations. The conformational stability of a new palladacycle shows a promising utility in a homochiral state as a matrix for the diverse processes of chiral recognition.

Experimental Section

General: ^{1}H- and ^{31}P-NMR spectra were recorded with a Varian VXR-400 spectrometer operating at the frequencies 400 and 161.9 MHz for ^{1}H and ^{31}P nuclei, respectively. The measurements were carried out at ambient temperature in $CDCl_3$ solutions (unless otherwise indicated). The proton chemical shifts are reported in parts per million relative to TMS as internal standard; the ^{31}P chemical shifts are given relative to H_3PO_4 as an external reference. The assignment of signals was performed on the basis of homonuclear decoupling, NOE experiments and spectral simulation. − IR spectra were recorded with a UR-250 spectrometer.

Solvents: Acetonitrile was distilled under argon from P_2O_5 and then from K_2CO_3; benzene, hexane and ether were dried with the appropriate drying agents and then distilled under argon from Na; anhydrous MeOH was prepared by distillation from MgOMe; dichloromethane was passed through a short Al_2O_3 column and distilled under argon; CCl_4 was refluxed in the presence of P_2O_5 and distilled; acetone of highest purity, and [D_1]chloroform (from Aldrich) were used as received; [D_5]pyridine was dried with 4-Å molecular sieves and distilled from KOH.

Reagents: Sodium acetate trihydrate was dehydrated by heating at 400°C; triphenylphosphane was purified by twofold recrystallization from a benzene/hexane mixture; hydroxylamine hydrochloride was used as received; lithium tetrachloropalladate was prepared according to a published procedure[6] and carefully dried in vacuo (3 Torr) over P_2O_5; palladium(II) acetate was purchased from Aldrich and used as received.

Starting Compounds: *tert*-Butyl phenyl ketone oxime was prepared by heating of pivalophenone[77] (12.80 g, 79 mmol) with hydroxylamine hydrochloride (6.05 g, 87 mmol) in the presence of $AcONa\cdot 3H_2O$ (11.8 g, 87 mmol) in aqueous methanol according to a published procedure;[78] after recrystallization from EtOH, the oxime was isolated in an 88% yield (17.93 g); m.p. 163−164°C. − ^{1}H NMR ($CDCl_3$): δ = 1.15 (s, 9 H, *t*Bu), 7.12 (dd, $^3J_{HH}$ = 7.9 Hz, $^4J_{HH}$ = 1.5 Hz, 2 H, *ortho-H* of Ph group), 7.33−7.45 (m, 3 H, *meta-H* and *para-H* of Ph group), 9.25 (br. s, 1 H, O*H*).

Racemic α-*tert*-Butylbenzylamine (HL^1) was prepared by reduction of *tert*-butyl phenyl ketone oxime (16.68 g, 0.094 mmol) under conditions previously described[79] in a yield of 72% (11.06 g, 0.068 mmol); b.p. 108−109°C/18 Torr; ^{1}H NMR ($CDCl_3$): δ = 0.91 (s, 9 H, *t*Bu), 1.40 (br. s, 2 H, NH_2), 3.69 (s, 1 H, α-C*H*), 7.21−7.32 (m, 5 H, Ph).

Synthesis of Cyclopalladated Compounds: All reactions were performed under argon in anhydrous solvents. Reactions were monitored by means of TLC on Silufol plates using an ether/heptane (5:1) mixture as eluent (unless otherwise indicated). In the case of μ-acetato complex formation, its conversion into the μ-chloro analogue by AcO^-/Cl^- metathesis (by treatment of a test probe of reaction mixture with LiCl solution in MeOH) was undertaken before spotting on the TLC plate. Dimeric complexes obtained were purified (unless otherwise indicated) using flash chromatography on a "dry" column[80][81] (Silpearl, *d* = 2.5 cm, *h* = 3.5 cm) with the eluents' polarity increasing (ether/heptane mixtures in the ratios from 1:10 up to 10:1 and then pure ether).

Di-μ-chlorobis[2-{1-amino-2,2-dimethylpropyl}phenyl-*C*,*N*]-dipalladium (II) (1a)

1. *ortho*-Palladation with Palladium(II) Acetate: i) Palladium acetate (0.206 g, 0.918 mmol) was added to racemic α-*tert*-butylbenzylamine HL^1 (0.150 g, 0.919 mmol) in methanol (5 mL) and the reaction mixture was stirred for 24 h at room temp. A solution of lithium chloride (0.190 g, 4.48 mmol) in methanol (3 mL) was added and the mixture was stirred for 2 h and then filtered. The residue was washed with methanol, combined with the mother liquor, concentrated in vacuo, and redissolved in dichloromethane (10 mL). The solution formed was washed with water to remove inorganic components, dried with sodium sulfate and concentrated to a volume of 2−3 mL. Flash column chromatography gave the coordination complex **2a** (from the first fraction) as a pale yellow microcrystalline solid in a yield of 19% (0.0443 g, 0.088 mmol) after

recrystallization from a dichloromethane/hexane mixture. From the second fraction, the μ-Cl dimer **1a** was isolated as a lime-yellow amorphous powder in a yield of 70% (0.195 g, 0.321 mmol) after precipitation from benzene by hexane.

For dimer **1a**: m.p. 217−219°C (dec). − R_f = 0.54. − IR (nujol): $\tilde{\nu}$ = 3213, 3308 cm^{-1} [ν(NH_2)]; 740 cm^{-1} [δ(CH_{ar})]. − ^{1}H NMR ($CDCl_3$, isomeric mixture): δ = 1.14 (br. s, 9 H, *t*Bu), 2.87 and 4.03 (br. s, 2 H, N*H*$_2$), 3.62 and 3.66 (s, 1 H, α-C*H*), 6.72 (br. s, 1 H, C_6H_4), 6.89 (m, 2 H, C_6H_4), 7.19 (br. s, 1 H, C_6H_4). − $C_{22}H_{32}Cl_2N_2Pd_2$ (608.26): calcd. C 43.44, H 5.30, N 4.23; found C 43.85, H 5.29, N 4.61.

For coordination complex **2a**: m.p. 171−173°C, R_f = 0.92.

ii) The same reaction of palladium acetate (0.225 g, 1.00 mmol) and amine HL[1] (0.163 g, 1.0 mmol) conducted in methanol (5 mL) at 50°C required 1.5 h for completion. After the treatment of the reaction mixture as described above [i)] it afforded the dimer **1a** in a 68% yield (0.207 g, 0.340 mmol); m.p. 217−219°C (dec), R_f = 0.54 (ether/heptane, 5:1); R_f = 0.44 (benzene/acetone, 7:1). − $C_{22}H_{32}Cl_2N_2Pd_2$: calcd. C 43.44, H 5.30, N 4.23; found C 43.40, H 5.35, N 4.27. − Under these conditions the coordination complex **2a** was formed in trace quantities.

iii) In a similar way, the reaction of palladium acetate (0.281 g, 1.25 mmol) and amine HL[1] (0.204 g, 1.25 mmol) was performed in acetone (10 mL). After heating at 50°C for 50 h and treatment of the reaction mixture as described above [i)], dimer **1a** was isolated in a yield of 68% (0.258 g, 0.424 mmol); m.p. 219−221°C (dec), R_f = 0.54.

iv) The interaction of palladium acetate (0.212 g, 0.944 mmol) and ligand HL[1] (0.154 g, 0.943 mmol) in benzene (7 mL) at room temp. afforded, after the stirring for 24 h and the treatment of reaction mixture as described above [i)] the dimer **1a** in a 43% yield (0.123 g, 0.202 mmol); m.p. 217−219°C (dec), R_f = 0.54. Under these conditions the coordination complex **2a** was isolated in a 41% yield (0.097 g, 0.193 mmol): m.p. 172−173°C, R_f = 0.92.

2. *ortho*-Palladation with Lithium Tetrachloropalladate(II): Racemic α-*tert*-butylbenzylamine (0.150 g, 0.919 mmol) in methanol (20 mL) was added to a mixture of lithium tetrachloropalladate (0.255 g, 0.973 mmol) and excess of sodium acetate (0.232 g, 2.83 mmol) in methanol (20 mL). The reaction mixture was stirred at room temp. for 23 h; after overnight storage, it was filtered and the residue was washed with methanol and then dichloromethane. The combined organic solutions were concentrated in vacuo and redissolved in dichloromethane (10 mL). Chromatographic separation using a dry column (Silpearl, d = 2.5 cm, h = 5 cm, ether/hexane from 1:10 up to 10:1 and then pure ether) and recrystallization as described above [i)] gave dimer **1a** as a limon−yellow amorphous powder in a yield of 50% (0.140 g, 0.230 mmol) from the second fraction. The mixture of diastereomeric coordination complexes (*R*,*R*)*/(*R*,*S*)-**2a** in an approximately 1:1 ratio (^{1}H-NMR data) was isolated from the first fraction in a 43% yield based on the ligand (0.100 g, 0.198 mmol); one of diastereomers was separated from this mixture by recrystallization from benzene/hexane and then from dichloromethane/hexane in a yield of 12% (0.0286 g, 0.057 mmol) as a pale yellow microcrystalline solid.

For **1a**: m.p. 217−219°C (dec), R_f = 0.54. − $C_{22}H_{32}Cl_2N_2Pd_2$ (608.26): calcd. C 43.44, H 5.30, N 4.23; found C 43.51, H 5.55, N 4.36.

For (*R*,*R*)*-**2a**: m.p. 171−173°C, R_f = 0.92. − IR (nujol): $\tilde{\nu}$ = 3310, 3230 cm^{-1} [br., ν(NH_2)], 750, 790 [δ(CH_{ar})]; (CCl_4): $\tilde{\nu}$ = 3310, 3233 cm^{-1} [br., ν(NH_2)]. − For ^{1}H-NMR data of the individual diastereomer **2a** see Table 1. − $C_{22}H_{34}Cl_2N_2Pd$ (503.85): calcd. C 52.44, H 6.80, N 5.56; found C 52.73, H 6.73, N 5.76.

^{1}H NMR of mixture of diastereomers (*R*,*R*)*/(*R*,*S*)-**2a** ($CDCl_3$): δ = 0.81 (s, 18 H, *t*Bu), 0.82 (s, 18 H, *t*Bu), 3.15 (br. t, 2 H, N*H*), 3.19 (br. t, 2 H, N*H*), 3.67 (br. m, 4 H, N*H*), 3.74 (m, 4 H, α-C*H*), 7.04 (m, 8 H, *ortho*-*H* of Ph groups), 7.26 (m, 12 H, *meta*- and *para*-*H* of Ph groups).

[2-{1-Amino-2,2-dimethylpropyl}phenyl-*C*,*N*]chloro([D$_5$pyridine)]-palladium(II) (3a) was generated in situ by the addition of 2−3 drops of [D_5]pyridine to a solution of dimer **1a** in $CDCl_3$ in an NMR tube. For ^{1}H-NMR data of complex **3a** see Table 1.

[2-{1-Amino-2,2-dimethylpropyl}phenyl-*C*,*N*]chloro(triphenylphosphane)palladium (II) (4a) was prepared by treatment of dimeric complex **1a** (0.100 g, 0.164 mmol) with triphenylphosphane (0.086 g, 0.33 mmol) in benzene (15 mL). The reaction mixture was stirred for 40 min at room temp. and concentrated to dryness. Recrystallization from dichloromethane/hexane and then from dichloromethane/acetonitrile afforded the mononuclear adduct **4a** in

Table 4. Crystal data, data collection, structure solution and refinement parameters for [2-(1-amino-2,2-dimethylpropyl)phenyl-*C*,*N*]chloro(triphenylphosphane)palladium(II)·MeCN solvate **4a**

Empirical formula	$C_{31}H_{34}ClN_2PPd$
Formula weight	607.42
Colour, habit	Light yellow, prism
Crystal size [mm]	0.09 × 0.12 × 0.45
Crystal system	triclinic
Space group	$P\bar{1}$
Unit cell dimensions:	
a [Å]	10.112(2)
b [Å]	12.245(2)
c [Å]	12.939(3)
α [°]	90.88(3)
β [°]	111.45(3)
γ [°]	101.40(3)
V [Å^3]	1455.0(5)
Z	2
Density (calcd.) [g/cm^3]	1.386
Absorption coefficient [mm^{-1}]	0.806
F(000)	624
Diffractometer	Enraf−Nonius CAD-4
T [K]	293
Radiation λ [Å]	graphite-monochromated Mo-K_α (0.71073)
Scan mode	ω/2θ
Scan width [°]	1.2 + 0.35 tan(θ)
Min/max scan rate [°/min]	2/8
θ range [°]	2.22−24.97
Index ranges	$-12 \le h \le 11$, $-14 \le k \le 14$, $0 \le l \le 15$
Reflections collected	4696
Independent reflections	4486 [R(int) = 0.0326]
Absorption correction	empirical (Ψ scan)
Min. and max. transmission	0.7365 and 0.9643
Decay correction	none
Solution method	direct methods (SHELX-86)
Refinement method	full-matrix least-squares on F^2 (SHELXL-93)
Hydrogen treatment	all H atoms found in Fourier synthesis and refined using riding model
Data/restraints/parameters	4486/0/330
Goodness of fit on F^2	0.996
Final R indices [$I > 2\sigma(I)$]	R_1 = 0.0351, wR_2 = 0.0850
R indices (all data)	R_1 = 0.0654, wR_2 = 0.0941
Extinction coefficient	0.0000(5)
Largest diff. peak and hole [e × Å^{-3}]	0.583 and −0.682

a 79% yield (0.147 g, 0.260 mmol) as a colourless microcrystalline MeCN solvate, m.p. 208−209°C, R_f = 0.30 (Silufol, benzene/acetone, 7:1). − IR (CCl_4): $\tilde{\nu}$ = 3238 cm^{-1} (br.), 3260, 3302 cm^{-1} [$\nu(NH_2)$]. − For ^{1}H-NMR data of complex **4a** see Table 1. − $^{31}P\{^1H\}$ NMR (CH_2Cl_2): δ = 41.57 (s). − $C_{29}H_{31}ClNPPd \cdot C_2H_3N$ (607.47): calcd. C 61.29, H 5.64, N 4.61; found C 60.82, H 5.70, N 4.24.

X-ray Crystallography for Complex 4a: Details of the X-ray experiment are given in Table 5. The experimental data were collected with an ENRAF Nonius CAD4 diffractometer using graphite-monochomatized Mo-K_α radiation. Experimental reflections were corrected for Lorentz and polarization effects. The hydrogen atoms were found from a difference Fourier synthesis and included in the refinement using the "riding model" with B_{iso} equal to $1.5B_{eq}$ of the parent atom. The structure was refined in the anisotropic approximation for the non-hydrogen atoms. A solvent molecule of acetonitrile was found during the structure solution, which forms a hydrogen bond with the coordinated chloride ligand of the main complex. The structure was solved and refined using the SHELXS-86[82] and SHELXL-93[83] software. Crystallographic data (excluding structure factors) for the structure reported in this paper have been deposited with the Cambridge Crystallographic Data Centre as supplementary publication no. CCDC-104570. Copies of the data can be obtained free of charge on application to CCDC, 12 Union Road, Cambridge CB2 1EZ, UK [Fax: int. code + 44-1223/336-033; E-mail: deposit@ccdc.cam.ac.uk].

Acknowledgments

This work was supported in part by the Russian Foundation for Basic Research (grant 95-03-09227).

[1] M. Pfeffer, *Pure Appl. Chem*. **1992**, *64*, 335.
[2] A. D. Ryabov, *Synthesis* **1985**, 233−252.
[3] J. Chengebroyen, M. Pfeffer, C. Sirlin, *Tetrahedron Lett*. **1996**, *37*, 7263−7266.
[4] J. Vicente, J.-A. Abad, A. D. Frankland, M.-C. Ramirez de Arellano, *J. Chem. Soc., Chem. Commun*. **1997**, 959−960.
[5] J. F. Hartwig, *Synlett* **1997**, 329−340.
[6] A. C. Cope, E. C. Friedrich, *J. Am. Chem. Soc*. **1968**, *90*, 909−913.
[7] Y. Fuchita, H. Tsuchiya, A. Miyafuji, *Inorg. Chim. Acta* **1995**, *233*, 91−96.
[8] J. Vicente, I. Saura-Liamas, M. G. Palin, P. G. Jones, *J. Chem. Soc., Dalton Trans*. **1995**, 2535−2539.
[9] J. Albert, J. Granell, A. Luque, J. Minguez, R. Moragas, M. Font-Bardia, X. Solans, *J. Organomet. Chem*. **1996**, *522*, 87−95.
[10] J. Vicente, I. Saura-Liamas, M. G. Palin, P. G. Jones, M. C. R. de Arellano, *Organometallics* **1997**, *16*, 826−833.
[11] Y. Fuchita, K. Yoshinaga, Y. Ikeda, J. Kinoshita-Kawashima, *J. Chem. Soc., Dalton Trans*. **1997**, 2495−2499.
[12] A. Avshu, R. D. O′Sullivan, A. W. Parkins, *J. Chem. Soc., Dalton Trans*. **1983**, 1619−1624.
[13] J. Vicente, I. Saura-Liamas, P. G. Jones, *J. Chem. Soc., Dalton Trans*. **1993**, 3619−3624.
[14] B. N. Cockburn, D. V. Howe, T. Keating, B. F. G. Johnson, J. Lewis, *J. Chem. Soc., Dalton Trans*. **1973**, 404−410.
[15] V. V. Dunina, O. A Zalevskaya, V. M. Potapov, *J. Gen. Chem. USSR* (*Engl. Transl.*) **1984**, *54*, 389−397.
[16] V. V. Dunina, O. A Zalevskaya, I. P. Smolyakova, V. M. Potapov, *J. Gen. Chem. USSR* (*Engl. Transl.*) **1986**, *56*, 674−684.
[17] L. G. Kuz′mina, O. Yu. Burtseva, M. A. Porai-Koshitz, V. V. Dunina, O. A. Zalevskaya, V. M. Potapov, *J. Gen. Chem. USSR* (*Engl. Transl.*) **1989**, *59*, 2525−2534.
[18] V. V. Dunina, N. S. Gulyukina, E. B. Golovan′, I. Yu. Nalimova, A. A. Koksharova, I. P. Beletskaya, *Organomet. Chem. USSR* (*Engl. Transl.*) **1993**, *6*, 36−46.
[19] V. V. Dunina, N. S. Gulyukina, I. V. Byakova, Yu. F. Oprunenko, I. P. Beletskaya, *Russ. J. Org. Chem*. (*Engl. Transl.*) **1994**, *30*, 1497−1506.
[20] V. V. Dunina, L. G. Kuz′mina, E. B. Golovan′, O. N. Gorunova, Yu. K. Grishin, *J. Organomet. Chem*., to be submitted.
[21] J. Albert, J. Granell, J. Minguez, G. Muller, D. Sainz, P. Valegra, *Organometallics* **1997**, *16*, 3561−3564.
[22] A. D. Ryabov, *Chem. Rev*. **1990**, *90*, 403−424.
[23] A. J. Canty, G. van Koten, *Acc. Chem. Res*. **1995**, *28*, 406−413.
[24] T. Yagyu, S.-i. Aizawa, Sh. Funahashi, *Bull. Chem. Soc. Jpn*. **1998**, *71*, 619−629.
[25] J. Dehand, M. Pfeffer, *C. R. Acad. Sci. Paris, Ser. C* **1975**, *281*, 363−366.
[26] H. Onoue, J. Moritani, *J. Organomet. Chem*. **1972**, *43*, 431−436.
[27] I. Jardine, F. J. McQuillin, *Tetrahedron Lett*. **1972**, 459−461.
[28] A. G. J. Ligtenbard, E. K. van den Beuken, A. Meetsma, N. Veldman, W. J. J. Smeets, A. L. Spek, B. L. Feringa, *J. Chem. Soc., Dalton Trans*. **1998**, 263−270.
[29] V. V. Dunina, O. A. Zalevskaya, V. M. Potapov, *Russ. Chem. Rev*. (*Engl. Transl.*) **1988**, *57*, 434−473 and refs. therein.
[30] A. L. Seligson, W. C. Trogler, *J. Am. Chem. Soc*. **1991**, *113*, 2520−2527.
[31] J. K. M. Sanders, J. D. Mersh, *Progr. NMR Spectrosc*. **1982**, *15*, 353−400.
[32] L. J. Bellami, *The Infrared Spectra of Complex Molecules*, J. Wiley, London, New York, **1963**, chapter 5.
[33] V. V. Dunina, V. P. Kislyi, N. S. Gulyukina, Yu. K. Grishin, I. P. Beletskaya, *Organomet. Chem. USSR* (*Engl. Transl.*) **1992**, *5*, 1297−1305.
[34] C. E. Barclay, G. Deeble, R. J. Doyle, Sh. A. Elix, G. Salem, T. L. Jones, S. B. Wild, A. C. Willis, *J. Chem. Soc., Dalton Trans*. **1995**, 57−65.
[35] R. J. Doyle, G. Salem, A. C. Willis, *J. Chem. Soc., Dalton Trans*. **1997**, 2713−2723.
[36] D. G. Allen, G. M. McLaughlin, G. B. Robertson, W. L. Steffen, G. Salem, S. B. Wild, *Inorg. Chem*. **1982**, *21*, 1007−1014.
[37] G. Salem, S. B. Wild, *Inorg. Chem*. **1983**, *22*, 4049−4054.
[38] J. W. L. Martin, J. A. L. Palmer, S. B. Wild, *Inorg. Chem*. **1984**, *23*, 2664−2668.
[39] Q. Jiang, H. Ruegger, L. M. Venanzi, *J. Organomet. Chem*. **1995**, *488*, 233−240.
[40] Y. Fuchita, H. Tsuchiya, *Inorg. Chim. Acta* **1993**, *209*, 229−230.
[41] V. V. Dunina, E. B. Golovan′, N. S. Gulyukina, A. V. Buyevich, *Tetrahedron: Asymmetry* **1995**, *6*, 2731−2746.
[42] V. V. Dunina, E. B. Golovan′, V. V. Pedchenko, A. A. Borisenko, I. P. Beletskaya, *Organomet. Chem. USSR* (*Engl. Transl.*) **1992**, *5*, 1121−1129.
[43] V. V. Dunina, E. B. Golovan′, *Tetrahedron: Asymmetry* **1995**, *6*, 2747−2754.
[44] V. V. Dunina, M. Yu. Kazakova, Yu. K. Grishin, O. R. Malyshev, and E. I. Kazakova, *Russ. Chem. Bull*. (*Engl. Transl.*) **1997**, N7, 1375−1384.
[45] A. Bondi, *J. Phys. Chem*. **1964**, *68*, 441−451.
[46] L. G. Kuz′mina, Yu. T. Struchkov, O. A. Zalevskaya, V. V. Dunina, V. M. Potapov, *J. Gen. Chem. USSR* (*Engl. Transl.*) **1987**, *57*, 2499−2507.
[47] B.-H. Aw, S. Selvaratnam, P.-H. Leung, N. H. Rees, W. McFarlane, *Tetrahedron: Asymmetry* **1996**, *7*, 1753−1762.
[48] P.-H. Leung, S. Selvaratnam, C. R. Cheng, K. F. Mok, N. H. Rees, W. McFarlane, *J. Chem. Soc., Chem. Commun*. **1997**, 751−752.
[49] A. J. Deeming, I. P. Rothwell, M. B. Hursthouse, L. New, *J. Chem. Soc., Dalton Trans*. **1978**, 1490−1496.
[50] P. W. Clark, S. F. Dyke, *J. Organomet. Chem*. **1985**, *281*, 389−396.
[51] J. Albert, J. M. Cadena, J. Granell, *Tetrahedron: Asymmetry* **1997**, *8*, 991−994.
[52] N. W. Alcock, J. M. Brown, D. I. Hulmes, *Tetrahedron: Asymmetry* **1993**, *4*, 743−756.
[53] N. W. Alcock, D. I. Hulmes, J. M. Brown, *J. Chem. Soc., Chem. Commun*. **1995**, 395−397.
[54] R. Annunziata, S. Cenini, F. Demartin, G. Palmisano, S. Tollari, *J. Organomet. Chem*. **1995**, *496*, C1−C3.
[55] V. V. Dunina, L. G. Kuz′mina, A. G. Parfyonov, Yu. K. Grishin, *Tetrahedron: Asymmetry* **1998**, *9*, 1917−1921.
[56] K. Tani, H. Tashiro, M. Yoshida, Ts. Yamagata, *J. Organomet. Chem*. **1994**, *469*, 229−236.
[57] P. W. Clark, S. F. Dyke, *J. Organomet. Chem*. **1984**, *276*, 421−430.

[58] S. Y. M. Chooi, M. K. Tan, P.-H. Leung, K. F. Mok, *Inorg. Chem*. **1994**, *33*, 3096−3103.
[59] S. Y. M. Chooi, T. S. A. Hor, P.-H. Leung, K. F. Mok, *Inorg. Chem*. **1992**, *31*, 1494−1500.
[60] P.-H. Leung, A. C. Willis, S. B. Wild, *Inorg. Chem*. **1992**, *31*, 1406−1410.
[61] M. Pabel, A. C. Willis, S. B. Wild, *Inorg. Chem*. **1996**, *35*, 1244−1249.
[62] S. Y. M. Chooi, S.-Y. Siah, P.-H. Leung, K. F. Mok, *Inorg. Chem*. **1993**, *32*, 4812−4818.
[63] D. C. R. Hockless, P. A. Gugger, P.-H. Leung, R. C. Mayadunne, M. Pabel, S. B. Wild, *Tetrahedron* **1997**, *53*, 4083−4094.
[64] H. Gunter, *NMR Spectroscopy − Basic Principles, Concepts, and Applications in Chemistry*, John Wiley, Chichester, **1995**, p. 115.
[65] H. Jendralla, Ch. H. Li, E. Paulus, *Tetrahedron: Asymmetry* **1994**, *5*, 1297−1320.
[66] W. Lesueur, E. Solari, C. Floriani, A. Chiesi-Villa, C. Rizzoli, *Inorg. Chem*. **1997**, *36*, 3354−3362.
[67] M.-C. Lagunas, R. A. Gossage, W. J. J. Smeets, A. L. Spek, G. van Koten, *Eur. J. Inorg. Chem.* **1998**, 163−168.
[68] M. Brookhart, M. L. H. Green, *J. Organomet. Chem*. **1983**, *250*, 395−408.
[69] T. C. Jones, A. J. Nielson, C. E. Rickard, *Aust. J. Chem*. **1984**, *37*, 2179−2192.
[70] J.-M. Valk, T. D. W. Claridge, J. M. Brown, *Tetrahedron: Asymmetry* **1995**, *6*, 2597−2610.
[71] G. Chelucci, M. A. Cabras, A. Saba, A. Sechi, *Tetrahedron: Asymmetry* **1996**, *7*, 1027−1032.
[72] H. Doucet, J. M. Brown, *Tetrahedron: Asymmetry* **1997**, *8*, 3775−3784.
[73] S. Gladiali, S. Pulacchini, D. Fabbri, M. Manassero, M. Sansoni, *Tetrahedron: Asymmetry* **1998**, *9*, 391−395.
[74] V. V. Dunina, O. A. Zalevskaya, I. P. Smolyakova, V. M. Potapov, L. G. Kuz′mina, Yu. T. Struchkov, L. N. Reshetova, *J. Gen. Chem. USSR* (*Engl. Transl.*) **1986**, *56*, 1164−1175.
[75] L. G. Kuz′mina, Yu. T. Struchkov, V. V. Dunina, O. A. Zalevskaya, V. M. Potapov, *J. Gen. Chem. USSR* (*Engl. Transl.*) **1987**, *57*, 599−609.
[76] V. V. Dunina, L. G. Kuz′mina, M. Yu. Kazakova, Yu. K. Grishin, Yu. A. Veits, E. I. Kazakova, *Tetrahedron: Asymmetry* **1997**, *8*, 2537−2545.
[77] J. H. Ford, C. D. Thompson, C. S. Marvel, *J. Am. Chem. Soc*. **1935**, *57*, 2619−2623.
[78] G. A. Tsatsas, *Ann. Chim., Ser. 12* **1946**, *1*, 342−394.
[79] P. Billon, *Ann. Chim., Ser. 10* **1927**, *7*, 314−384.
[80] J. T. Sharp, I. Gosney, A. G. Rowley, *Practical Organic Chemistry − A student handbook of techniques*, London − New York, Chapman and Hall, **1989**, chapter 4.2.2d.
[81] L. M. Harwood, *Aldrichim. Acta* **1985**, *18*, 25.
[82] G. M. Sheldrick, *Acta Crystallogr*. **1990**, *A46*, 467.
[83] G. M. Sheldrick, *SHELXL-93 − Program for the Refinement of Crystal Structures*, University of Göttingen, Germany, **1993**.

Received October 27, 1998
[I98367]