A new method for modification of *CN*-palladacycles*

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The reaction of benzylaminate *CN*-palladacycle with chlorine dioxide was found to produce the 3-chlorine-substituted analog through the formal insertion of chlorine into the Pd—C bond followed by repeated *ortho*-palladation of the modified ligand. The structure of the resulting dimeric complex was confirmed by X-ray diffraction study of its triphenylphosphine derivative. A comparison of the ^{1}H NMR spectra of the phosphine adducts of the starting and chlorinated complexes shows high conformational stability of the new palladacycle. Advantages of the new route to conformational stabilization of labile palladacycles are discussed.

Key words: palladacycles, chlorination, chlorine dioxide, X-ray diffraction analysis, conformation of palladacycles, histograms.

The reactions of cyclopalladated complexes (CPCs) at the Pd—C bond are of interest as an elegant approach to the regioselective organic synthesis.[1,2] Although there are numerous publications concerning this problem, studies of oxidation of palladacycles (formal insertion of oxygen into the Pd—C bond) are rather scarce. Organic peracids,[3—9] lead(IV) acetate,[10] *tert*-butyl hydroperoxide,[11,12] molybdenum peroxides,[13,14] or iodosoarenes[15,16] are used as oxidizing agents in these reactions, whereas simpler oxidants (for example, H_2O_2) are unsuitable for this purpose.[6] The efficiency of these processes often strongly depends on the structure of palladacycle. In some cases, oxidation can be achieved only in the presence of a catalyst.[11,12] Until recently, the range of substrates has been limited to cyclopalladated derivatives of achiral ligands, such as azoarenes,[5,6,8,9,15—17] tertiary benzylamines,[4,11—14] and aliphatic ketone oximes.[10]

Two factors have stimulated our studies in this area. First, oxidation of chiral palladacycles could provide a new route to the synthesis of optically active amino alcohols, which are known to be efficient ligands in enantioselective catalysis.[18—20] Second, it is of interest to perform this reaction with the use of simpler and readily available oxidants. We decided to use chlorine dioxide[21] as a cheap commercially available reagent, which often allows one to perform highly selective oxidation of both organic[22—26] and main-group organometallic compounds (B, Al, and Mg).[27,28] Reactions with chlorine dioxide result predominantly in oxidation of substrates. However, several examples of the formation of mixtures of the oxidation and chlorination products of organic substrates were documented.[29—34] In this connection, it was necessary to elucidate the features of the behavior of this reagent with respect to palladacycles.

In the present study, we examined the reactions of the simplest chiral *CN*-palladacycle, *viz.*, the *N,N*-dimethyl-α-methylbenzylamine derivative, with chlorine dioxide.

* Dedicated to Academician N. S. Zefirov on the occasion of his 70th birthday.

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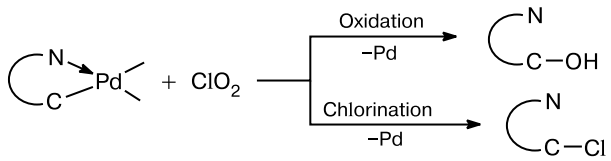
The preliminary results of our study have been presented at a conference.[35]

Results and Discussion

The reactions of palladacycles with oxidants generally lead to the formal insertion of oxygen into the Pd—C bond giving rise to hydroxy,[3—6,8,9,11,12,14—16] alkoxy,[13,14] or acyloxy derivatives[10,36,37] of the starting substrates isolated as free ligands or their complexes with palladium(II). Although these reactions are performed with either chloro-bridged dimeric CPCs[4—6,10—12,14,15] or chloride forms of their mononuclear derivatives,[3,8,9,13,16] the insertion of chlorine into the Pd—C bond of the palladacycle is generally not observed. However, the reactions of chlorides of benzylaminate *CN*- and *CNN*-palladacycles with molybdenum peroxide was demonstrated[14] (GLC analysis) to give (along with standard hydroxy or alkoxy derivatives) alternative chlorination products. For example, oxidation of the pyridine adduct of *ortho*-palladated *N,N*-dimethyl-α-methylbenzylamine in methanol afforded a chlorination product in trace amounts (4%), but its yield was increased to 22% when the reaction was performed in dichloromethane and it was further increased to 61% in the presence of an excess of chloride ions (3.2 equiv. of $[Et_3NBn]Cl$).[14]

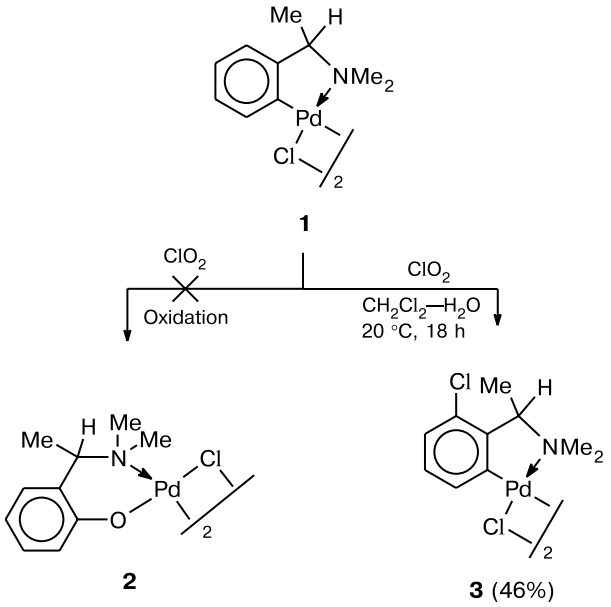
Taking into account these results and the known features of the reactivity of chlorine dioxide, we considered the following two possible pathways of its reactions with palladacycles at the Pd—C bonds: hydroxylation and chlorination (Scheme 1), the former process being assumed as a more probable pathway.

Scheme 1



Oxidation of chloro-bridged dimeric CPCs generally affords dinuclear coordination compounds with *N,O*-chelated aminophenoxides of the general formula $[\{(\kappa^2\text{-}N^{\frown}O)Pd(\mu\text{-}Cl)\}_2]$ as primary products.[5,11,12,15,16] Monochlorination products are sometimes isolated (without demetallation) as free ligands in reactions of palladacycles with gaseous chlorine.[38,39] However, repeated cyclopalladation of the modified ligand, which occurs through the intermediate formation of new μ-chloride dinuclear CPC, was observed in some cases.[17,40] According to these results, whatever the pathway may be, the reaction of complex **1** with chlorine dioxide would be expected to form a chloro-bridged dimeric palladium(II) complex, *viz.*, either a coordination compound with *N,O*-chelated aminophenoxide (**2**) or a cyclometallated complex with chlorinated *CN*-palladacycle (**3**) (Scheme 2).

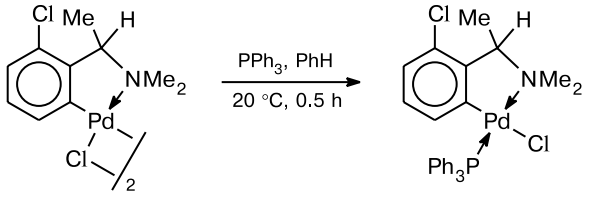
Scheme 2



Initially, we used racemic μ-chloride dimer **1** in studies of the reaction of CPC with chlorine dioxide. The reaction was carried out under mild conditions, at room temperature in a two-phase dichloromethane—water system with the use of a stoichiometric amount of ClO_2 (as a ~0.05 *M* aqueous solution) in the absence of light to avoid radical decomposition of the reagent.[41] A chlorinated complex was isolated in moderate yield (46%) by chromatography. In addition, a complex mixture of unidentified oxidation products was formed.

Some experimental data provide evidence that chlorination rather than oxidation is the major process under these conditions. The resulting light-yellow complex differs in the color from known bright-red aminophenoxide analogs **2**.[12] In addition, the elemental composition of this complex differs substantially from the calculated composition of dimer **2** (by more than 2% of the carbon content). Both characteristics are quite consistent with those expected for structure **3**, which is a chlorinated analog of the starting CPC **1**. Both alternative reaction products would be expected to have dinuclear structures. Hence, with the aim of confirming the structure of the complex by spectroscopy, it was transformed into a mononuclear phosphine derivative with hypothetical structure **4** using the standard chloride-bridge cleavage reaction (Scheme 3).

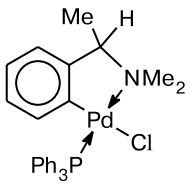
Scheme 3



3 **4** (90%)

The ^{1}H NMR spectrum of phosphine complex **4** also confirms its cyclopalladated structure and the presence of a substituent in the phenylene fragment. The retention of the Pd—C bond in mononuclear complex **4** (and, consequently, in the starting dimer **3**) is evidenced primarily by upfield shifts (under the influence of anisotropy of the PPh rings) of the signals for two aromatic protons, H(6) and H(5), nearest to this bond (to δ 6.21 and 6.29, respectively; Fig. 1) compared to those in the spectra of trialkylphosphine derivatives of *ortho*-palladated complexes. In the latter spectra, the proton H(6) generally gives a signal at δ 7.0—7.6.[42] These shifts of the signals are consistent with the *trans*-(*P,N*) geometry of phosphine adduct **4**. The observed spin-spin coupling constant between the proton H(6) and the phosphorus nucleus ($J_{H,P}$ = 6.2 Hz) (coupling occurs partially through space) also confirms the cyclopalladated structure of complex **4** and its *trans*-(*P,N*) configuration.

The presence of a substituent in the phenylene fragment is evident from the fact that the ^{1}H NMR spectrum of complex **4** shows only three well-resolved signals in the aromatic proton resonance region (δ 6.1—6.9, see Fig. 1) instead of four signals characteristic of benzylaminate palladacycles containing the unsubstituted Ph ring,[43—45] including the closest analog **5**. The multiplicities of the resonance lines of three aromatic protons in the spectrum of complex **4** (see Fig. 1) and the ^{1}H—^{1}H and ^{1}H—^{31}P coupling constants (see the Experimental section) are also consistent with the vicinal arrangement of these protons.



5

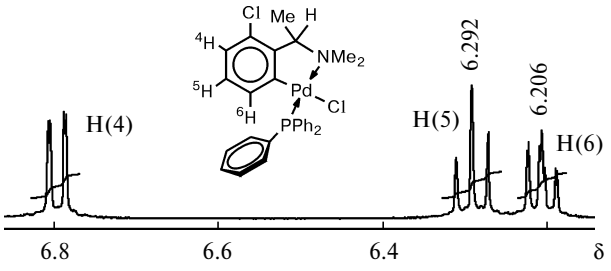


Fig. 1. Fragment of the ^{1}H NMR spectrum of phosphine complex **4** in the region of resonance of the protons of the palladated phenylene ring.

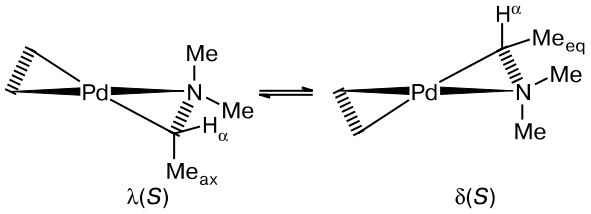


Fig. 2. Chiral conformations of the five-membered α-methylbenzylaminate *CN*-palladacycle, λ(*S*) and δ(*S*).

The presence of the chlorine atom at position 3 of the phenylene fragment is evidenced by small shifts of the signals for the aromatic protons in the ^{1}H NMR spectrum of complex **4** compared to those observed for analog **5**: Δδ for the protons H(4), H(5), and H(6) are −0.03, −0.09, and −0.13, respectively, which agree well with the known increments for the chlorine atom in monosubstituted benzenes (from −0.02 to −0.06 ppm), but they are approximately an order of magnitude smaller than those expected for oxygen-containing substituents (from −0.4 to −0.5 ppm for OH).[46]

The fact that the chlorine atom is in the immediate vicinity of the side chain of the benzylaminate ligand is indirectly confirmed by the downfield shifts of the signals for the protons of the α-CH and α-Me groups compared to their positions in the ^{1}H NMR spectrum of triphenylphosphine-containing compound **5** derived from dimer **1** (Δδ 0.2 and 0.13, respectively).

Conformational stabilization of the new palladacycle is the most important consequence of the appearance of the chlorine atom adjacent to the side chain of the benzylaminate ligand. Spectroscopic and structural studies of chiral cyclopalladated derivatives of benzylamines showed that their simplest representative (present in dimer **1** and its phosphine adduct **5**) is conformationally labile[47—50] and exists in solution as an equilibrium mixture of two conformers* (Fig. 2).

To the contrary, the 1-naphthyl-[48,51,52] and α-*tert*-butyl-substituted[43—45] analogs of compound **1** are conformationally stable and exist predominantly in one λ(*S*) conformation, in which a substituent in the α-benzyl position of the side chain is in an axial orientation. This property of palladacycles is to a large extent responsible for their efficiency in chiral recognition.[53]

To estimate the influence of the chlorine atom at position 3 of the phenylene fragment on the conformation of the palladacycle, we performed repeated ^{1}H NMR spectroscopic study of PPh_3 adduct **5**.[54,55] A comparison of the spectroscopic characteristics of phosphine complex **4** and its analog **5** shows that the new palladacycle exists

* Hereinafter, the conformational analysis of racemic complexes was performed for the (*S*) enantiomer.

predominantly in the λ(*S*) conformation in which the α-Me group in the side chain is in an axial orientation. The efficiency of spin-spin coupling between the α-methine proton and ^{31}P of the phosphine ligand generally serves as the main criterion for estimating the conformational state of this type of palladacycles. According to the principles of NMR spectroscopy,[46,56] this parameter is determined primarily by the degree of coplanarity of the chain consisting of four bonds separating these nuclei ($^{1}H—C—N—Pd—^{31}P$). The range of possible variations of this parameter can be determined as follows. The values ($^{4}J_{H,P}$ = 6—8 Hz) for PPh_3 derivatives of *ortho*-palladated benzaldimines with the α-methine proton in a strictly equatorial orientation can serve as the upper limit of this range.[57] From general considerations,[56] this upper limit is somewhat overestimated due to the presence of the double bond in the chain of bonds separating the interacting nuclei ($^{1}H—C=N—Pd—^{31}P$). The lower limit of this range ($^{4}J_{H,P}$ = 0 Hz) is determined by the absence of signs of α-$CH^{\cdots 31}P$ spin-spin coupling for the *quasi*-axial methine proton in the spectra of phosphine adducts of α-unsubstituted benzylaminate palladacycles.[58—60] The constant $^{4}J_{H,P}$ = 6.3 Hz for the α-CH proton in complex **4**, which is close to the upper limit of this range, indicates that this proton is in a nearly equatorial position. This corresponds to the *quasi*-axial orientation of the α-Me group at the carbon stereocenter in the λ(*S*) conformation (see Fig. 2, *a*). For comparison, it should be noted that the constant $^{4}J_{H,P}$ for the α-methine proton decreases to 4.7 Hz in the spectrum of complex **5** containing no substituents at position 3, which indicates that the palladacycle exists as an equilibrium mixture of two conformers, λ(*S*) and δ(*S*), in comparable amounts.

The shift of the equilibrium between two conformers, *viz.*, δ(*S*) and λ(*S*), of the palladacycle in adduct **4** toward one of these conformers can be additionally confirmed by the following facts. The signals for the protons of two diastereotopic NMe groups are shifted in the opposite directions compared to their positions in the spectrum of analog **5** containing the unsubstituted phenylene ring. The downfield shift of one of these signals (Δδ +0.08) indicates that this proton approaches the coordination plane, *e.g.*, to an anisotropy region of the chloride ligand bound to palladium, whereas the signal of another NMe group is shifted upfield (Δδ −0.12), which is associated with the fact that it moves away from the Pd—Cl bond. These shifts are quite significant taking into account the statistical factor. The conclusion that the palladacycle in adduct **4** exists predominantly in one of two possible conformations is also confirmed by the fact that the difference between the coupling constants between the protons of two NMe groups and the phosphorus nucleus in the ^{1}H NMR spectrum of **4** ($^{4}J_{H,P}$ = 3.6 and 1.7 Hz) is almost twice as large as that for analog **5** containing the unsubstituted phenylene fragment ($^{4}J_{H,P}$ = 3.1 and 2.1 Hz). This is also evidence that one NMe group in 3-chloro-substituted complex **4** is in a more equatorial orientation, whereas another NMe group is in a more axial orientation. Therefore, the spectroscopic data are indicative of substantial conformational stabilization of the palladacycle as a result of the appearance of the chlorine atom at position 3 of the aromatic ring.

The structure of new dimeric cyclopalladated complex **3** was confirmed by X-ray diffraction analysis of its triphenylphosphine derivative **4**. To estimate the influence of the chlorine atom in the phenylene ring on the conformation of the palladacycle, we carried out X-ray diffraction analysis of its unsubstituted analog **5**. The molecular structures of racemic complexes **4** and **5** are shown in Fig. 3. Selected bond lengths, bond angles, and torsion

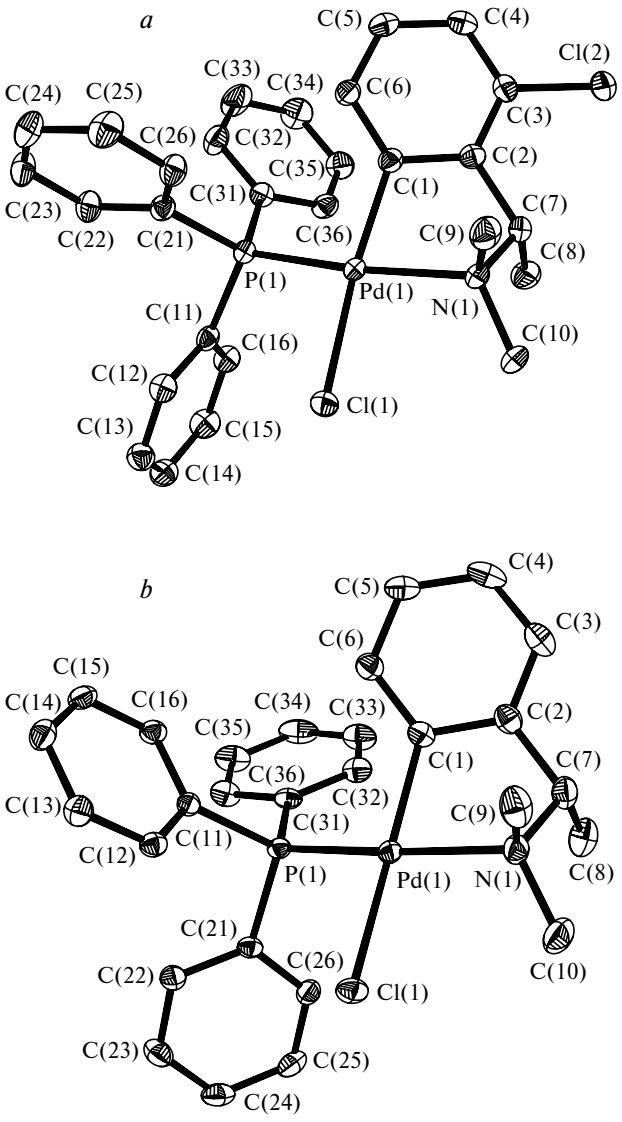


Fig. 3. Molecular structure and the atomic numbering scheme for the (*S*) enantiomers of triphenylphosphine complexes **4** (*a*) and **5** (*b*).

angles are given in Tables 1, 2, and 3, respectively. Phosphine adduct **4** crystallizes in the chiral space group $P2_12_12_1$, and the unit cell contains four molecules of **4** of an (*S*) configuration. Analog **5** crystallizes in the non-centrosymmetric space group *Pbca*, and the unit cell contains eight molecules of (*S*) and (*R*) configurations in an equal ratio.

Table 1. Selected bond lengths in the structures of complexes **4** and **5**

Bond	*d*/Å	
	Complex **4**	Complex **5**
Pd(1)—P(1)	2.2606(5)	2.2474(6)
Pd(1)—Cl(1)	2.3814(4)	2.4052(6)
Pd(1)—C(1)	2.007(2)	1.998(2)
Pd(1)—N(1)	2.158(2)	2.160(2)
P(1)—C(21)	1.817(2)	1.828(2)
P(1)—C(11)	1.822(2)	1.818(2)
P(1)—C(31)	1.832(2)	1.828(2)
N(1)—C(9)	1.490(3)	1.490(4)
N(1)—C(10)	1.495(2)	1.479(4)
N(1)—C(7)	1.503(3)	1.512(3)
C(1)—C(2)	1.412(3)	1.414(3)
C(2)—C(7)	1.514(3)	1.507(4)
C(7)—C(8)	1.521(3)	1.518(4)
C(7)—H(7)	0.98(2)	1.03(3)
Cl(2)—C(3)	1.762(2)	

Table 2. Selected bond angles in the structures of complexes **4** and **5**

Angle	ω/deg	
	Complex **4**	Complex **5**
C(1)—Pd(1)—N(1)	80.57(7)	80.32(9)
C(1)—Pd(1)—P(1)	91.95(5)	94.60(7)
N(1)—Pd(1)—P(1)	169.62(5)	170.47(6)
C(1)—Pd(1)—Cl(1)	172.28(6)	168.22(7)
N(1)—Pd(1)—Cl(1)	92.25(4)	94.16(6)
P(1)—Pd(1)—Cl(1)	95.53(2)	92.25(2)
C(21)—P(1)—Pd(1)	114.20(7)	111.80(8)
C(11)—P(1)—Pd(1)	113.32(7)	111.88(7)
C(31)—P(1)—Pd(1)	112.00(7)	118.95(8)
C(9)—N(1)—C(10)	106.7(2)	107.1(2)
C(9)—N(1)—C(7)	110.1(2)	108.5(2)
C(10)—N(1)—C(7)	110.6(2)	111.6(2)
C(9)—N(1)—Pd(1)	108.4(1)	110.2(2)
C(10)—N(1)—Pd(1)	117.6(1)	114.9(2)
C(7)—N(1)—Pd(1)	103.4(1)	104.4(2)
C(2)—C(1)—Pd(1)	111.6(1)	113.0(2)
C(1)—C(2)—C(7)	117.6(2)	117.2(2)
N(1)—C(7)—C(2)	106.5(2)	105.5(2)
N(1)—C(7)—C(8)	111.9(2)	111.9(2)
C(2)—C(7)—C(8)	110.1(2)	111.3(2)
N(1)—C(7)—H(7)	108.00(1)	—
C(2)—C(7)—H(7)	107.00(1)	—
C(21)—P(1)—C(11)	105.05(9)	105.9(1)
C(21)—P(1)—C(31)	106.90(9)	101.5(1)
C(11)—P(1)—C(31)	104.63(9)	105.6(1)

Table 3. Selected torsion angles in the structures of complexes **4** and **5**

Angle	τ/deg	
	Complex **4**	Complex **5**
Parameters of palladacycle		
C(1)—Pd(1)—N(1)—C(7)	−38.54(0.12)	36.34(16)
Pd(1)—N(1)—C(7)—C(2)	44.75(0.17)	−45.1(2)
C(1)—C(2)—C(7)—N(1)	−30.18(0.23)	34.2(3)
Pd(1)—C(1)—C(2)—C(7)	−3.06(0.22)	−3.3(3)
N(1)—Pd(1)—C(1)—C(2)	23.42(0.14)	−18.88(17)
C(1)—C(2)—C(3)—Cl(2)	−173.85(0.14)	—
Orientations of substituents in palladacycle		
C(1)—Pd(1)—N(1)—C(9)	78.26(0.13)	−80.01(18)
C(1)—Pd(1)—N(1)—C(10)	−160.73(0.18)	158.9(2)
C(1)—C(2)—C(7)—C(8)	91.30(0.22)	−87.4(3)
Orientation of PPh rings		
C(1)—Pd(1)—P(1)—C(11)	153.12(0.09)	82.76(10)
C(1)—Pd(1)—P(1)—C(21)	−86.64(0.09)	−158.64(10)
C(1)—Pd(1)—P(1)—C(31)	35.04(0.09)	−40.83(11)

X-ray diffraction data unambiguously confirmed the cyclopalladated structure of complex **4** and the presence of the chlorine atom in the phenylene fragment of the benzylaminate ligand in the *ortho* position with respect to the side chain (see Fig. 3, *a*).

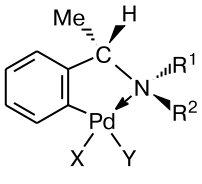
As can be seen from Tables 1 and 2, the geometric parameters of molecule **4** are rather similar to those of molecule **5**. The Pd—C, Pd—N, Pd—P, and Pd—Cl bond lengths in complexes **4** and **5** fall in the ranges typical of triphenylphosphine adducts of five-membered α-arylalkylaminate palladacycles. Both complexes have slightly tetrahedrally distorted square-planar structures. The angles between the {NPdC}/{PPdCl} planes are 7.55(8) and 13.04°, respectively.* In both complexes, the coordination environment of the palladium(II) atom has the *trans*-(*P,N*) geometry characteristic of this type of compounds. In both complexes, the distance between the aromatic proton H(6), which is the nearest one to the site of metallation, and the phosphorus atom of the auxiliary ligand is shortened (2.98(2) and 3.03(3) Å, respectively) and is smaller than or close to the sum of the van der Waals radii of these atoms (~3.0 Å).[61] This confirms that the through-space $^1H(6)\cdots^{31}P$ interaction can occur. The orientation of the PPh ring nearest to the H(6) atom with respect to this atom is consistent with the effects, which are observed in the ^1H NMR spectra and are associated with anisotropy of the aromatic rings of the auxiliary ligand. In the structures of complexes **4** and **5**, the dis-

* Hereinafter, the first and second parameters refer to complexes **4** and **5**, respectively.

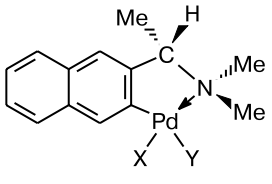
tance between the H(6) atom and the center of the nearest PPh ring is 3.31 and 3.59 Å, respectively.

A comparison of the conformational features of two palladacycles in two maximum similar complexes in the crystalline state is of most interest. Both palladacycles adopt a twisted envelop conformation with the nitrogen atom deviating from the mean plane through the other four atoms. The angles between the {PdNC(7)} and {PdC(1)C(2)C(7)} planes in the structures of complexes **4** and **5** have similar values (46.0(1) and 44.7(1)°, respectively). Both palladacycles are also characterized by approximately the same degree of nonplanarity, which is described by the averaged absolute values of the intrachelate torsion angles of 28.0 and 27.6°, respectively. Both palladacycles adopt the λ(*S*) conformation as evidenced from the negative values of the C(1)—Pd—N—C(7) torsion angles (−38.5(1) and −36.3(2)°, respectively; see Table 3). Quantitative differences are observed only in the orientation of the substituents in the side chain of the benzylaminate palladacycles. A comparison of the angles between the corresponding bonds and the normal to the mean coordination plane (*mcpl*) shows that the position of the N—Me_{eq} bond in the chlorinated palladacycle of adduct **4** is somewhat closer to equatorial (69.2 and 62.9°), the orientations of the axial N—Me_{ax} bond being almost the same in both complexes (angles are 4.0 and 4.5°). This is consistent with the above-mentioned difference in the spectroscopic parameters of two complexes.

It is not surprising that the λ(*S*) conformation of the starting (nonchlorinated) palladacycle in complex **5** is stabilized in the crystal lattice taking into account its flexibility. Among an extensive series of crystallographically characterized derivatives of α-methylbenzylaminate palladacycle containing chiral or achiral additional ligands, we can find complexes containing palladacycles either in the λ(*S*) or δ(*S*) conformation, depending on the requirements imposed by either an auxiliary ligand or the crystal lattice. This is quite evident from the distribution histogram of the inclination angles of the $C_α$—C(Me) bond with respect to the normal to *mcpl* presented in Fig. 4. The histogram was constructed using the data on α-methylbenzylaminate palladacycles of type $\mathbf{A^1}$ and their 2-naphthyl analogs of type $\mathbf{A^2}$, which contain no substituents at position 3 of the metallated phenylene ring, taken from the Cambridge Structural Database (CSD).*



$\mathbf{A^1}$



$\mathbf{A^2}$

* The CSD Version 5.25 (August 2004 Release) was used.

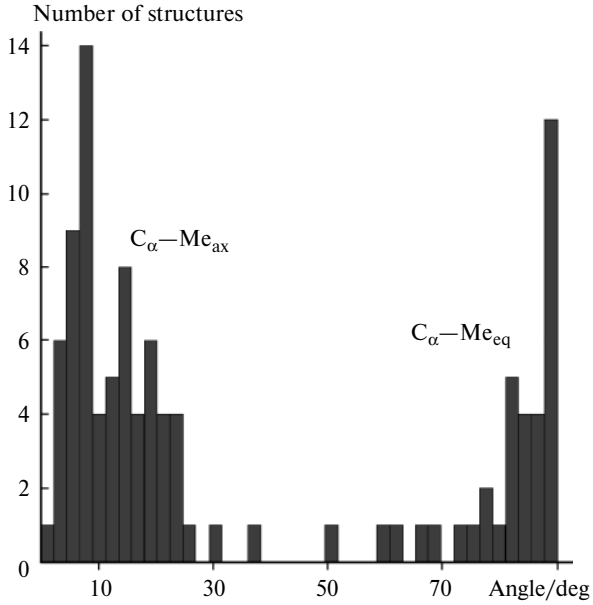


Fig. 4. Distribution histogram of the angles between the $C_α$—C(Me) bond and the normal to *mcpl* for derivatives of α-methylbenzylaminate and α-(2-naphthyl)ethylaminate palladacycles of type **A** containing no substituents at the C(3) atom of the metallated phenylene fragment (64 entries, 103 fragments).

Of 103 nonequivalent palladacycles of type **A**, only 68 palladacycles adopt the λ(*S*) conformation with the axial α-Me group (angles between the $C_α$—C(Me) bond and the normal to *mcpl* vary in the range of ~0—40°). In other 35 fragments comprising one-third of all data, the metallacycle adopts the opposite δ(*S*) conformation with the equatorial α-Me group (angles are ~50—90°). This statistics is quite consistent with the above-given NMR data for complex **5**.

For comparison, another histogram (Fig. 5) represents the distribution of the inclination angles of the Me group at the α-C* stereocenter for diverse derivatives of modified α-methylbenzylaminate palladacycles containing a particular substituent at position 3 of the metallated phenylene fragment. This set of compounds includes cyclopalladated derivatives of α-(1-naphthyl)ethylamines ($\mathbf{B^1}$ type), α-(9-phenanthryl)ethylamine ($\mathbf{B^2}$ type), and α,2,5-trimethylbenzylamine ($\mathbf{B^3}$ type). In these types of complexes, palladacycles are characterized by high conformational stability in solutions. As expected, essentially all data for these complexes fall within a narrow range of inclination angles of the bond with the axial α-Me group (~0—28°) corresponding to the λ(*S*) conformation of palladacycles. The only exception is the five-coordinate derivative of *N,N*-dimethyl-α-(1-naphthyl)ethylaminate palladacycle of type $\mathbf{B^1}$ containing the macrocyclic diiminodiarsine ligand, for which this parameter increases to ~46 or ~68° depending on the chosen base of the polyhedron.

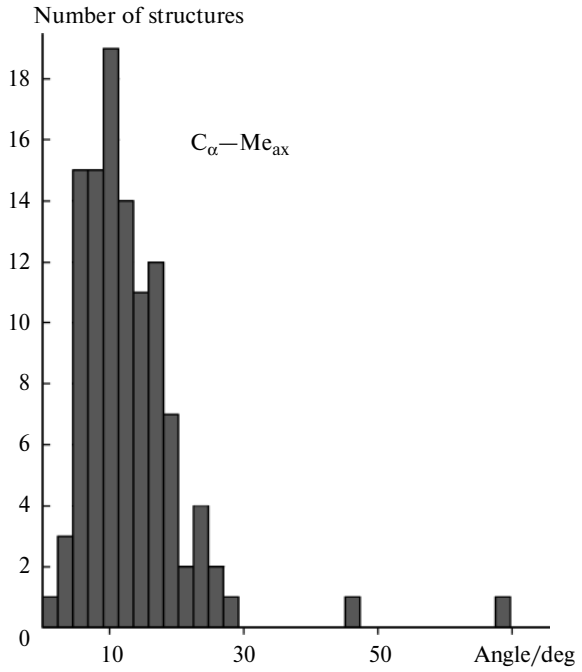
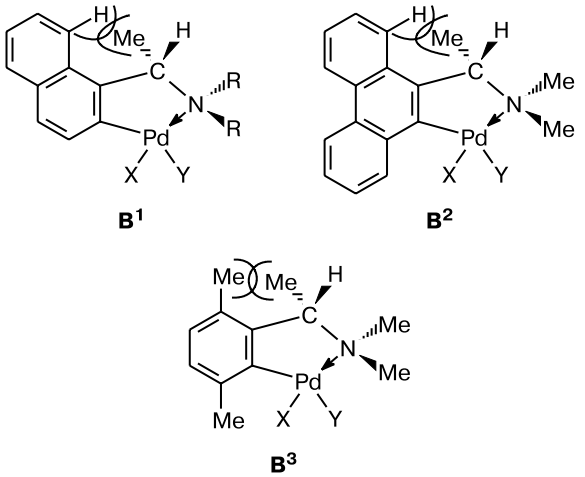


Fig. 5. Distribution histogram of the angles between the C_α—C(Me) bond and the normal to *mcpl* for derivatives of α-(1-naphthyl)ethylaminate and other palladacycles of type **B** containing a substituent at the C(3) atom of the metallated phenylene fragment (74 entries, 99 fragments).

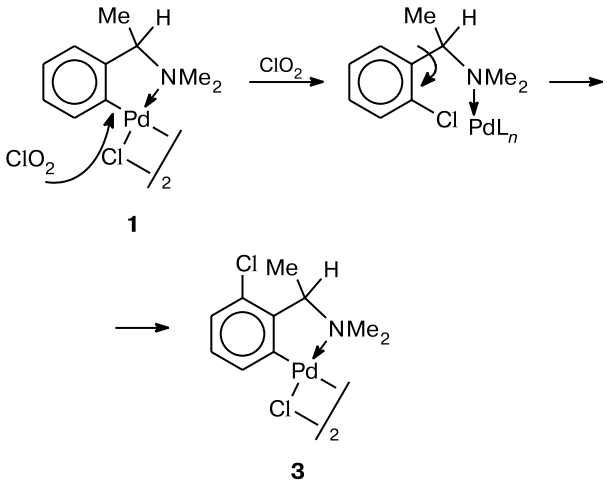


B[1] **B**[2] **B**[3]

The above results deserve detailed consideration in two aspects.

First, we found that the cheap and commercially available reagent chlorine dioxide acts as a regioselective chlorinating agent rather than as an oxidant with respect to palladacycles. Since the direct replacement of the hydrogen atom at position 3 of the aromatic ring seems to be improbable because of both electronic and steric factors, it is reasonable to assume that the process involves chlorination at the Pd—C bond to give *ortho*-chloro-substituted tertiary benzylamine followed by its repeated cyclopalladation (Scheme 4).

Scheme 4



The preliminary results of experiments with an optically active cyclopalladated derivative of prochiral benzhydrylamine confirm this scheme.[62] This pathway is quite consistent with the known precedents of the formation of mixtures of polychlorinated azobenzenes through repeated cyclopalladation of the ligands modified in previous steps. The latter process provides the basis for a procedure of catalytic chlorination of azobenzene in the presence of palladium(II) chloride.[17,40]

Second, an important result is that the reaction with chlorine dioxide produces new CPC rather than a free modified ligand or its coordination compound with palladium. This reaction opens a new way for conformational stabilization of the readily available optically active (but dynamically labile) α-methylbenzylaminate palladacycle due to steric control by the bulky chlorine atom located in the vicinity of the side chain. This is of importance for the chiral recognition ability of palladacycle. For comparison, it should be noted that the known procedure for the synthesis of *ortho*-chloro-substituted (*S*)-α-methylbenzylamine (through *N*-silylation of primary amine, *ortho*-lithiation, and subsequent chlorination with hexachloroethane)[63] involves many steps and is very laborious (total yield of 56%). An alternative approach to conformational stabilization of α-methylbenzylaminate palladacycles based on a structural modification of the starting ligands, which has been recently developed,[64,65] is also more complicated. This approach requires the separation of enantiomers either at the stage of racemic primary amine (for example, in the case of the replacement of the Ph ring with the 9-phenanthryl fragment in CPC of type **B**[2])[65] or at the stage of a cyclopalladated complex prepared from

this amine (in the case of the insertion of 2,5-dimethyl groups into the Ph ring in CPC of type **B**[3]).[64]

Experimental

The ^{1}H and ^{31}P{^{1}H} NMR spectra were recorded on a Varian VXR-400 spectrometer (400 and 169.1 MHz, respectively) in $CDCl_3$ at room temperature. The chemical shifts in the ^{1}H NMR spectra were determined relative to the internal standard (Me_4Si), and the chemical shifts in the ^{31}P NMR spectra were measured relative to the external standard (H_3PO_4). The assignment of the signals was made using the homonuclear ^{1}H-^{1}H spin-spin decoupling technique The melting point was measured using the melting point indicator EM-MGU No. 49 in a sealed capillary tube. The course of the reactions was monitored and the purities of the compounds were checked by TLC on Silufol UV-254. The complexes were preparatively isolated by dry column chromatography[66] on silica gel Silpearl. The solvents were purified by standard methods: chloroform and dichloromethane were passed through a column with neutral Al_2O_3 (Brockmann activity II, L 40/250) and distilled; benzene was refluxed over sodium metal and distilled; acetone (special purity grade) and hexane were distilled.

Commercial chlorine dioxide as an aqueous solution (3 g L^{-1}) was used without additional purification; its concentration was determined by titration according to a known method.[67] Triphenylphosphine was twice recrystallized from a benzene—hexane mixture. The racemic dimer of di-μ-chlorobis{2-(1-dimethylaminoethyl)phenyl-*C,N*}dipalladium(II) (**1**) was synthesized according to a known procedure.[54]

(*R,S*)-Di-μ-chlorobis[3-chloro-2-(1-dimethylaminoethyl)phenyl-*C,N*]dipalladium(II) (3). An aqueous ClO_2 solution (15.8 mL) was added to a solution of complex **1** (0.1000 g, 0.172 mmol) in dichloromethane (5 mL), after which the color of the organic layer changed from yellow to red. The reaction mixture was stirred at room temperature for 18 h in the dark. The organic layer was separated and washed with water (2×3 mL). The aqueous fraction was extracted with CH_2Cl_2 (4 mL). The combined organic extracts were concentrated to dryness. After chromatographic purification on a column (h = 4 cm, d = 2.5 cm, hexane and benzene as the eluents) complex **3** was isolated as an amorphous light-yellow powder in a yield of 0.0538 g (46%), m.p. (with decomp.) 241—243 °C; R_f 0.77 (benzene—acetone, 25 : 1). Found (%): C, 37.40; H, 4.33; N, 4.21. $C_{20}H_{26}Cl_4N_2Pd_2$. Calculated (%): C, 37.01; H, 4.04; N, 4.32. ^{1}H NMR ($CDCl_3$), δ: 3.80 (m, 1 H, α-CH); 1.81 (d, 3 H, α-Me, $^3J_{H,H}$ = 6.0 Hz); 2.61 and 2.91 (both s, 3 H each, NMe); 7.05 (m, 1 H, H(6)); 6.80 (t, 1 H, H(5), $^3J_{5,4}$ = 7.9 Hz, $^3J_{5,6}$ = 7.9 Hz); 6.96 (d, 1 H, H(4), $^3J_{4,5}$ = 7.9 Hz, $^4J_{4,6}$ = 0.8 Hz).

(*R,S*)-Chloro-[(3-chloro-2-(1-dimethylaminoethyl)phenyl-*C,N*](triphenylphosphine-*P*)palladium(II) (4). An excess of PPh_3 (0.0181 g, 0.0679 mmol) was added to a solution of complex **3** (0.0201 g, 0.0309 mmol) in benzene (2 mL). The reaction mixture was stirred at room temperature for 30 min and concentrated to dryness. After chromatographic purification on a column (h = 4 cm, d = 2.5 cm, hexane, benzene, and benzene—acetone, 20 : 1, as the eluents), complex **4** was isolated as an amorphous almost colorless powder in a yield of 0.0328 g (90%), m.p. 205—208 °C; R_f 0.24 (benzene—acetone, 20 : 1). Found (%): C, 56.93; H, 4.65; N, 2.16. $C_{28}H_{28}Cl_2NPPd$. Calculated (%): C, 57.31; H, 4.81; N, 2.38. ^{31}P NMR ($CDCl_3$), δ: +37.96. ^{1}H NMR ($CDCl_3$), δ: 4.02 (dq, 1 H, α-CH, $^3J_{H,H}$ = 6.3 Hz, $^3J_{H,P}$ = 6.3 Hz); 1.93 (d, 3 H, α-Me, $^3J_{H,H}$ = 6.3 Hz); 2.73 (d, 3 H, NMe_{ax}, $^3J_{H,P}$ = 1.7 Hz); 2.85 (d, 3 H, NMe_{eq}, $^3J_{H,P}$ = 3.6 Hz); 6.21 (ddd, 1 H, H(6), $^3J_{5,6}$ = 7.7 Hz, $^4J_{4,6}$ =1.0 Hz, $J_{H,P}$ = 6.2 Hz); 6.29 (t, 1 H, H(5), $^3J_{5,4}$ = $^3J_{5,6}$ ≈ 7.7 Hz); 6.80 (dd, 1 H, H(4), $^3J_{4,5}$ = 7.7 Hz, $^4J_{4,6}$ = 1.0 Hz); 7.35 (m, 6 H, H_m, PPh_3); 7.41 (m, 3 H, H_p, PPh_3); 7.70 (m, 6 H, H_o, PPh_3, $^3J_{H,P}$ = 11.3 Hz).

(*R,S*)-Chloro-[2-(1-dimethylaminoethyl)phenyl-*C,N*](triphenylphosphine-*P*)palladium(II) (5) was synthesized according to the method described earlier for the (*S*) enantiomer.[55] After chromatographic purification on a column (h = 2.5 cm, d = 2.5 cm, elution with diethyl ether—hexane mixtures with a polarity gradient from 1 : 3 to 5 : 1), complex **5** was isolated as an amorphous light-yellow powder in 84% yield, m.p. (with decomp.) 205—207 °C; R_f 0.53 (benzene—acetone, 5 : 1). ^{1}H NMR ($CDCl_3$), δ: 3.82 (dq, 1 H, α-CH, $^3J_{H,H}$ = 6.5 Hz, $^3J_{H,P}$ = 4.7 Hz); 1.80 (d, 3 H, α-Me, $^3J_{H,H}$ = 6.5 Hz); 2.85 (d, 3 H, NMe_{ax}, $^3J_{H,P}$ = 2.1 Hz); 2.77 (d, 3 H, NMe_{eq}, $^3J_{H,P}$ = 3.1 Hz); 6.34 (ddd, 1 H, H(6), $^3J_{6,5}$ = 7.5 Hz, $^4J_{6,4}$ = 1.3 Hz, $J_{H,P}$ = 6.2 Hz); 6.38 (dt, 1 H, H(5), $^3J_{5,4}$ = $^3J_{5,6}$ ≈ 7.5 Hz); 6.83 (ddd, 1 H, H(4), $^3J_{4,5}$ = $^3J_{4,3}$ ≈ 7.5 Hz, $^4J_{4,6}$ = 1.3 Hz); 7.00 (dd,

Table 4. Crystallographic data, details of X-ray data collection, and characteristics of structure refinement of complexes **4** and **5**

Parameter	**4**	**5**
Molecular formula	$C_{28}H_{28}Cl_2N_1P_1Pd_1$	$C_{28}H_{29}Cl_1N_1P_1Pd_1$
Molecular weight	586.78	552.34
Temperature	120(2)	95(2)
Crystal system	Orthorhombic	Orthorhombic
Space group	$P2_12_12_1$	*Pbca*
a/Å	7.7195(1)	11.5040(8)
b/Å	16.4007(3)	17.167(1)
c/Å	20.7317(3)	25.160(2)
V/Å^3	2624.74(7)	4968.9(6)
Z	4	8
d_{calc}/g cm^{-3}	1.485	1.477
μ/mm^{-1}	0.988	0.935
F(000)	1192	2256
θ Scan range/deg	1.58—27.50	1.62—28.00
Ranges of indices	$-9 \le h \le 10$	$-15 \le h \le 15$
	$-21 \le k \le 17$	$-24 \le k \le 23$
	$-26 \le l \le 25$	$-34 \le l \le 35$
Number of measured/ independent reflections	18405/5997	50930/6000
R_{int}	0.0258	0.0717
Number of parameters in refinement	410	406
R_1 ($I \ge 2\sigma(I)$)	0.0193	0.0347
wR_2 (based on all reflections)	0.0465	0.0769
Goodness-of-fit on F^2	1.040	1.205
Flack parameter	−0.03(1)	—
Residual electron density (max/min)/e Å^{-3}	0.468/−0.305	0.509/−0.626

1 H, H(3), $^3J_{3,4}$ = 7.5 Hz, $^4J_{3,5}$ = 1.3 Hz); 7.35 (m, 6 H, H_m, PPh_3); 7.42 (m, 3 H, H_p, PPh_3); 7.73 (m, 6 H, H_o, $^3J_{H,P}$ = 11.4 Hz, PPh_3).

X-ray diffraction study. Crystals of complexes **4** and **5** suitable for X-ray diffraction study were grown by slow crystallization from benzene—dichloromethane—hexane and chloroform—heptane—hexane solvent systems, respectively. X-ray diffraction data sets were collected on a Bruker SMART diffractometer (Mo$K\alpha$ radiation, λ = 0.71073 Å, graphite monochromator). Crystallographic data, details of X-ray data collection, and characteristics of structure refinement for complexes **4** and **5** are given in Table 4. Absorption corrections were applied based on the intensities of equivalent reflections. The structures were solved by direct methods (SHELXS-86).[68] All non-hydrogen atoms were refined by the full-matrix least-squares method against F^2 with anisotropic displacement parameters (SHELXL-97).[69] The hydrogen atoms in both structures were located from difference Fourier maps and refined isotropically. The crystallographic data for the structures of compounds **4** and **5** were deposited with the Cambridge Structural Database (refcodes BANMAF and XOZPAD, respectively).

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