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Competition between sp^3 and sp^2 C–H bonds in cyclopalladation of *N*-methyl-α-*tert*-butylbenzylamine

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Abstract

Intramolecular palladation of the (sp^3)C–H bond of a *tert*-butyl group of *N*-methyl-α-*tert*-butylbenzylamine can be achieved in competition with (sp^2)C–H bond activation where both possible reactions are equally suitable for five-membered palladacycle formation. Activation of the (sp^3)C–H bond occurs with $PdCl_4^{2-}$ assisted by a secondary amino group as a heterodonor center in a benzylamine ligand; regioselective activation of the (sp^2)C–H bond was achieved with PdI_4^{2-}. To compare, cyclopalladation of the related tertiary amine occurs regioselectively to give *ortho*-palladated complex as the sole product. The structure of both regioisomeric complexes was confirmed by an X-ray study of their triphenylphosphine adducts. The conformational features of the two five-membered palladacycles is discussed on the base of the ^{1}H-NMR and X-ray data.

Keywords: Cyclopalladation; Benzylamines; Regioselectivity; Crystal structure; Palladacycle conformation; Nuclear Overhauser effect

1. Introduction

In cyclometallation chemistry, selectivity in activation of C–H bonds in ligands containing two or more sites for metallation is not well understood [1]. Experimental data on this subject is too limited for general conclusions to be made. The following reasons for regioselectivity have been discussed: (i) the specific precoordination type [2–4]; (ii) lowering in the activation energy of one site due to close approach of the corresponding C–H bond toward the metal center [5]; (iii) increase of C–H acidity of one of the C–H bonds [6], and (iv) the kinetic versus thermodynamic control of the reaction [7,8].

Among the diverse alternative systems studied to date only a few examples of competition between sp^3 and sp^2 carbon centers during the process of cyclopalladation are known. In these cases (sp^3)C–Pd bond formation was promoted by the following factors: (i) use of palladation agent of very low electrophilicity [9]; (ii) enhancement of the C–H acidity by the neighboring bipolar function due to the use of a more polar solvent [6]; (iii) the inclusion of the ligand C=N bond in the palladacycle [7,10]; (iv) bidentate coordination of ligand through heterodonor atoms resulting in close approach of the metal center to the (sp^3)C–H bond [4,11]. In the last mentioned case, the cyclometallation at the (sp^3)C–H site becomes to be a forced process.

This communication presents the results of our investigations of regioselectivity in intramolecular palladation of secondary amine, namely, *N*-methyl-α-*tert*-butylbenzylamine (HL^1).

2. Experimental

2.1. General conditions

All reactions were performed under an argon atmosphere. Benzene, toluene, Et_2O and hexane were freshly distilled from sodium; CH_2Cl_2 and $CHCl_3$ were purified

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chromatographically on a column of Al_2O_3 and then distilled; MeOH was refluxed over magnesium methoxide for 3 h and then distilled; AcOH was freshly freezed out; CD_2Cl_2 and $CDCl_3$ (from Aldrich) were kept over MS 4 Å; AcONa was dried over P_2O_5 in vacuo (10^{-2} mmHg) at 120°C. The chromatographic monitoring of reaction course and control for the compounds purity was performed by TLC on Silufol UV-254 after AcO^-/Cl^- anion metathesis if needed; silica gel L40/100 or Sealpearl were used for preparative column chromatography. The regioisomeric dimeric complexes **1a**/**2a** ratio was determined using ^{1}H-NMR data for their d_5-pyridine derivatives generated in situ.

^{1}H- and ^{31}P-NMR spectra were recorded with a Varian VXR-400 spectrometer operating at 400.0 and 161.9 MHz for ^{1}H and ^{31}P nuclei, respectively. The measurements were carried out at ambient temperature in $CDCl_3$ (unless otherwise indicated). The proton chemical shifts are presented in parts per million (ppm) relative to TMS as internal reference, J in Hz; the ^{31}P chemical shifts are given relative to 85% H_3PO_4 as an external standard. The signal assignment was performed using homonuclear ^{1}H–^{1}H spin–spin decoupling and differential NOE experiments.

2.2. Starting compounds

Palladium(II) acetate was prepared as reported previously [12] in a 90% yield, m.p. 205–206°C (dec.); Li_2PdCl_4 was obtained according to a published procedure [13] and dried over P_2O_5 in vacuo (10^{-2} mmHg) at 110°C (yield 95%); $PdCl_2$ was used as received from Aldrich.

Racemic *N*-methyl-α-*tert*-butylbenzylamine (HL^1) was prepared by the reported method [14] in a 50% yield, b.p. 102°C/15 mmHg. ^{1}H-NMR ($CDCl_3$): δ 0.915 (s, 9H, ^{t}Bu), 1.497 (br s, 1H, NH), 2.222 (s, 3H, NMe), 3.224 (s, 1H, α-CH), 7.26–7.31 (m, 5H, Ph); (CD_2Cl_2 [15]): δ 0.87 (s, 9H, ^{t}Bu), 1.38 (br s, 1H, NH), 2.15 (s, 3H, NMe), 3.18 (s, 1H, α-CH), 7.17–7.30 (m, 5H, Ph).

2.3. Cyclopalladation reactions

Di-μ-chlorobis{2-[2,2-dimethyl-1-(methylamino)-propyl]phenyl-*C*,*N*}dipalladium(II) (**1a**) and di-μ-chlorobis{2,2-dimethyl-3-phenyl-3-(methylamino)propyl-*C*,*N*} dipalladium(II) (**2a**). The identity of dimer samples obtained by different methods was confirmed by TLC for dimers and ^{1}H-NMR data for their d_5-pyridine derivatives.

(i) A solution of Li_2PdCl_4 (1.647 g, 6.29 mmol) in anhydrous MeOH (20 ml) was added to a mixture of racemic amine HL^1 (1.115 g, 6.29 mmol) and AcONa (2.580 g, 31.5 mmol) in absolute MeOH (30 ml). After stirring at room temperature (r.t.) for 40 h under an argon atmosphere, the reaction mixture was filtered, evaporated; the residue was extracted with $CHCl_3$ and purified chromatographically (column, l 25 cm, d 2.5 cm) using benzene and then consequently 20:1 and 10:1 benzene–acetone mixtures as eluents. A mixture of coordination complexes **3A** and **3B** in ca. 1:2 ratio was first eluted in a total yield of 3%, R_f 0.87 (benzene–acetone 10:1) and then the mixture of two regioisomeric CPC **1a**/**2a** in ca. 1:2 ratio was isolated in a total yield of 86%. After repeated column chromatography (Et_2O–hexane 10:1) and recrystallyzation from CH_2Cl_2–hexane and Et_2O–hexane, respectively, a fraction enriched to 80% (sp^3)-regioisomer **2a** and pure *ortho*-palladated dimer **1a** were obtained in yields of 20 and 60%, respectively. After repeated column chromatography of diastereomeric complexes **3A**/**3B** mixture (l 28 cm, d 1.0 cm, benzene–hexane 3:1) two diastereomeric racemates **3A** and **3B** were isolated.

For **1a**: m.p. 144–146°C, R_f 0.71 (Et_2O–hexane 10:1). Anal. Calc. for $C_{24}H_{36}Cl_2N_2Pd_2$: C, 45.30; H, 5.70; N, 4.40. Found: C, 45.37; H, 5.76; N, 4.17%. ^{1}H-NMR: δ 1.256 (s, 9H, α-^{t}Bu), 2.921 (d, 3H, $^3J_{HCNH}$ 6.3, NMe), 3.368 (s, 1H, α-CH), 3.59 (br m, 1H, NH); phenylene group: 6.87–6.89 (m, 2H, $C^3H + C^5H$), 6.951 (m, 1H, $^3J_{HH}$ 7.4, $^4J_{HH}$ 1.2, C^4H), 7.141 (br m, 1H, C^6H). For **2a**: R_f 0.76 (Et_2O–hexane 10:1).

For **3A**: m.p. 161–163°C, R_f 0.63 (benzene–hexane 10:1, two-fold elution). Anal. Calc. for $C_{24}H_{38}Cl_2N_2Pd$: C, 54.19; H, 7.20; N, 5.27. Found: C, 54.16; H, 7.33; N, 5.20%. ^{1}H-NMR (CD_2Cl_2, two sets of signals in ca. 3:2 ratio): for major isomer: δ 1.443 (s, 18H, ^{t}Bu), 2.513 (d, 6H, $^3J_{HCNH}$ 5.9, NMe), 3.580 (br m., 2H, NH), 3.935 (d, 2H, $^3J_{HCNH}$ 11.3, α-CH); for minor isomer: δ 1.441 (s, 18H, ^{t}Bu), 2.527 (d, 6H, $^3J_{HCNH}$ 5.4, NMe), 3.492 (br m, 2H, NH), 3.984 (d, 2H, $^3J_{HCNH}$ 11.2, α-CH); aromatic protons for both isomers: 7.11 (dd, 4H, *ortho*-H of Ph ring), 7.27–7.36 (m, 6H, *meta*-H and *para*-H of Ph ring).

For **3B**: m.p. 158–159°C, R_f 0.27 (benzene–hexane 10:1, two-fold elution). Anal. Calc. for $C_{24}H_{38}Cl_2N_2Pd$: C, 54.19; H, 7.20; N, 5.27. Found: C, 54.21; H, 7.37; N, 5.20%. ^{1}H-NMR (CD_2Cl_2, two sets of doubled signals in ca. 2:1 ratio): for major isomer (two sets of signals originated from nonequivalent ligands): δ 0.969 (s, 9H, ^{t}Bu) and 1.314 (s, 9H, ^{t}Bu); 1.84 (d, 3H, $^3J_{HCNH}$ 6.0, NMe) and 3.04 (d, 3H, $^3J_{HCNH}$ 6.0, NMe); 4.13 (br m, 2H, NH); 3.680 (d, 1H, $^3J_{HCNH}$ 11.0, α-CH) and 3.765 (d, 1H, $^3J_{HCNH}$ 11.0, α-CH); for minor isomer (two sets of signals from nonequivalent ligands): δ 0.963 (s, 9H, ^{t}Bu) and 1.230 (s, 9H, ^{t}Bu); 1.90 (d, 3H, $^3J_{HCNH}$ 6.0, NMe) and 3.06 (d, 3H, $^3J_{HCNH}$ 6.0, NMe); 4.00 (br m, 2H, NH); 3.67 (d, 1H, $^3J_{HCNH}$ 11, α-CH) and 3.87 (d, 1H, $^3J_{HCNH}$ 11, α-CH); aromatic protons for both isomers: 6.96–7.44 (10H, Ph).

(ii) Reaction of amine HL^1 (0.048 g, 0.27 mmol) with Li_2PdCl_4 (0.071 g, 0.27 mmol) and AcONa (0.111 g, 1.34 mmol) in 1:1 aqueous MeOH (6 ml) was con-

ducted at r.t. for 48 h. After standard treatment, chromatographic purification (column, *l* 15 cm, *d* 2.5 cm, 5:1 benzene–acetone) the regioisomer **1a**/**2a** mixture in ca. 4.5:1 ratio was obtained in a 65% yield.

(iii) A solution of Li_2PdCl_4 (0.0765 g, 0.292 mmol), amine HL[1] (0.052 g, 0.292 mmol), AcONa (0.120 g, 1.46 mmol) and KI (0.242 g, 1.46 mmol) in anhydrous MeOH (5 ml) was stirred at r.t. for 15 h[1], concentrated, diluted with acetone (5 ml) and 20% excess of $AgNO_3$ was added. After stirring for 1 h an excess of LiCl was added and stirring was continued for 1 h. Then reaction mixture was filtered, evaporated, the residue was extracted with $CHCl_3$ and purified chromatographically (column, *l* 15 cm, *d* 2.5 cm, 5:1 benzene–acetone) to give dimer **1a** of $>98\%$ regioisomeric purity in a yield of 62%.

(iv) A mixture of $PdCl_2$ (0.154 g, 0.87 mmol) and amine HL[1] (0.154 g, 0.87 mmol) in HMPA (2 ml) was stirred for 2 h at 60°C and then for 2 h at 110–115°C and treated with water. After extraction with $CHCl_3$, washing with 1 N HCl, H_2O and drying over Na_2SO_4, dimer formed was purified as in (ii) to give **1a** in a yield of ca. 30%.

(v) A solution of $Pd(OAc)_2$ (0.100 g, 0.45 mmol) and amine HL[1] (0.0789 g, 0.45 mmol) in glacial AcOH (5 ml) was stirred at 60°C for 4 h, filtered from Pd(0) formed (0.015 g), evaporated, and the residue was treated with LiCl (0.042 g, 1 mmol) in acetone. After stirring at r.t. for 15 min the reaction mixture was evaporated, and the residue was purified chromatographically (7:1 benzene–acetone) to give the mixture of regioisomers **1a**/**2a** in ca. 3:1 ratio in a total yield of 60%.

(vi) The solution of amine HL[1] (0.087 g, 0.49 mmol) and $Pd(OAc)_2$ (0.110 g, 0.49 mmol) in anhydrous benzene (10 ml) was stirred at r.t. (5 h), then at 60°C (3 h) and refluxed (2 h). Then it was evaporated, the residue redissolved in toluene (10 ml) and refluxed for 1.5 h. After AcO^-/Cl^- metathesis (as described under (v)) and purification (as in (ii))) the mixture of regioisomeric CPC **1a**/**2a** in ca. 4:1 ratio was isolated in the total yield of 70%.

2.4. Preparation of mononuclear adducts

2.4.1. Chloro(d_5-pyridine-N){2-(1-methylamino-2,2-dimethylpropyl)phenyl-C,N}palladium(II) (**4′**) and chloro(d_5-pyridine-N){(3-methylamino)-2,2-dimethyl-3-phenylpropyl-C,N}palladium(II) (**5′**)

A mixture of mononuclear complexes **4′**/**5′** in 2:1 ratio was generated in situ by dissolving a 2:1 mixture of dimers **1a**/**2a** in $CDCl_3$ in the presence of three to four drops of d_5-pyridine in an NMR tube directly.

For **4′**: ^{1}H-NMR: δ 1.26 (s, 9H, ^{t}Bu), 2.86 (d, 3H, $^3J_{HH}=6.3$ Hz, NMe), 3.35 (s, 1H, α-CH), 3.74 (br m, 1H, NH); aromatic protons ($CDCl_3$): 6.15 (d, 1H, $^3J_{HH}=7.6$, C^6H), 6.78 (dt, 1H, C^5H), 6.94 (dt, 1H, C^4H), 6.99 (d, 1H, C^3H); aromatic protons (CD_2Cl_2): 6.186 (dd, 1H, $^3J_{HH}=7.6$, $^4J_{HH}=1.2$, C^6H), 6.787 (ddd, 1H, $^3J_{HH}=7.6$, $^3J_{HH}=7.4$, $^4J_{HH}=1.6$, C^5H), 6.947 (ddd, 1H, $^3J_{HH}=7.4$, $^3J_{HH}=7.6$, $^4J_{HH}=1.2$, C^4H), 7.010 (dd, 1H, $^3J_{HH}=7.6$, $^4J_{HH}=1.6$, C^3H).

For **5′**: ^{1}H-NMR: δ 0.663 (s, 3H, CMe), 1.062 (s, 3H, CMe), 1.730 (d, 1H, $^2J_{HH}=8.3$, PdCH), 2.185 (d[2], 1H, $^2J_{HH}=9.2$, PdCH), 2.624 (d, 3H, $^3J_{HH}=5.9$, NMe), 3.343 (d, 1H, $^3J_{HCNH}=11.9$, α-CH), 4.18 (br dq, 1H, NH); aromatic protons: 7.09 (br d, 2H, $^3J_{HH}=7.8$, *ortho*-H), 7.22–7.37 (m, 3H, *meta*-H and *para*-H).

2.5. Chloro(pyridine-N){2-(1-methylamino-2,2-dimethylpropyl)phenyl-C,N}palladium(II) (**4**) and chloro(pyridine-N){(3-methylamino)-2,2-dimethyl-3-phenylpropyl-C,N}palladium(II) (**5**)

A solution of a 2:1 mixture of dimers **1a**/**2a** (0.0555 g, 0.0872 mmol) and anhydrous pyridine (0.041 g, 0.52 mmol, 0.04 ml) in benzene (2 ml) was stirred for 0.5 h at r.t., concentrated in vacuo and the residue was treated with hexane. The precipitate formed was filtered, washed with hexane and recrystallized slowly from the mixture of chloroform–hexane under cooling. At this stage a mixture of two different kinds of crystals of **4** and **5** was precipitated. *ortho*-Palladated adduct **4** was separated by hand as large colorless transparent cubic crystals in the yield of 42% (0.0291 g, 0.073 mmol). Mononuclear derivative **5** was obtained as a colorless crystalline plates in a yield of 19% (0.0133 g, 0.034 mmol)[3].

For **4**: m.p. 168–170°C (dec.). Anal. Calc. for $C_{17}H_{23}ClN_2Pd$: C, 51.40; H, 5.84; N, 7.05. Found: C, 50.76; H, 5.80; N, 6.71%. ^{1}H-NMR: δ 1.296 (s, 9H, ^{t}Bu), 2.901 (d, 3H, $^3J_{HCNH}=6.3$, NMe), 3.435 (s, 1H, α-CH), 3.774 (br m, 1H, NH); aromatic protons: 6.181 (dd, 1H, $^3J_{HH}=7.6$, $^4J_{HH}=1.2$, C^6H), 6.821 (ddd, 1H, $^3J_{HH}=7.6$, $^3J_{HH}=7.4$, $^4J_{HH}=1.8$, C^5H), 6.975 (ddd, 1H, $^3J_{HH}=7.4$, $^3J_{HH}=7.6$, $^4J_{HH}=1.2$, C^4H), and 7.011 (dd, 1H, $^3J_{HH}=7.6$, $^4J_{HH}=1.8$, C^3H); protons of pyridine ligand: 7.383 (m, 2H, β-H), 7.829 (m, 1H, γ-H), and 8.856 (m, 2H, α-H).

For **5**: m.p. 90–92°C (dec.). Anal. Calc. for $C_{17}H_{23}ClN_2Pd\cdot CHCl_3$: C, 41.86; H, 4.68; N, 5.42. Found: C, 42.92; H, 4.88; N, 5.63%.

[1] The TLC-monitoring of reaction course (ether–hexane, 2:1) was performed after a treatment of a small portion of reaction mixture with an excess of $AgNO_3$ and then with an excess of LiCl in acetone.

[2] The doublet signal is slightly broadened by $^4J_{HH}$ coupling.

[3] Regioisomeric adducts **4** and **5** were identified by means of TLC after conversion of testing samples into the corresponding dimers **1a** and **2a** via treatment with dilute HCl in a CH_2Cl_2/H_2O system.

2.6. Chloro(triphenylphosphine-P){2-[2,2-dimethyl-1-(methylamino)propyl]phenyl-C,N}palladium(II) (6) and chloro(triphenylphosphine-P){2,2-dimethyl-3-phenyl-3-(methylamino)propyl-C,N}palladium(II) (7)

A slight excess of triphenylphosphine (0.2531 g, 0.965 mmol) was added to a suspension of a 2:1 mixture of regioisomeric dimers **1a**/**2a** (0.3011 g, 0.473 mmol) in benzene (35 ml). After the reaction mixture was stirred for 1 h at r.t., it was concentrated in vacuo and the complexes formed were precipitated with hexane to give a crude regioisomers **6**/**7** mixture in the yield of 88% (0.4924 g, 0.848 mmol). It was recrystallized two times from a benzene–heptane mixture to obtain a chromatographically pure *ortho*-palladated adduct **6** in the yield of 24% (0.1318 g, 0.227 mmol). The mother liquor enriched by (sp^3)-regioisomer **7**, was slowly recrystallized three times from the mixture of benzene–ether under cooling to give an analytically pure complex **7** in the yield of 13% (0.0714 g, 0.123 mmol).

For **6** adduct: m.p. 212–214°C (dec.), R_f 0.42 (ether–hexane mixture in 5:1 ratio). ^{31}P-NMR: δ 37.90 ppm (s); ^{1}H-NMR spectra of adduct **6** is actually identical to that presented below.

For **7** adduct: m.p. 208–210°C (dec.), R_f 0.33 (ether–hexane 5:1 mixture). Anal. Calc. for $C_{30}H_{33}ClNPPd$: C, 62.08; H, 5.73; N, 2.41. Found: C, 62.23; H, 5.78; N, 2.24%. ^{31}P-NMR: δ 32.36 ppm (s); ^{1}H-NMR: δ 0.578 (s, 3H, CMe^{ax}), 1.015 (s, 3H, CMe^{eq}), 1.140 (dd, 1H, $^2J_{HH} = 9.6$, $^3J_{HP} = 9.4$, CH^{eq}), 1.804 (d, 1H, $^2J_{HH} = 9.6$, CH^{ax}), 2.808 (dd, 3H, $^3J_{HCNH} = 5.9$, $^4J_{HP} = 3.0$, NMe), 3.368 (d, 1H, $^3J_{HCNH} = 12.1$, α-CH), 3.763 (br ddq, 1H, $^3J_{HNCH} = 12.1$, $^3J_{HNMe} = 6.0$, $^3J_{HP} = 4.2$, NH); aromatic protons: 7.134 (d, 2H, $^3J_{HH} = 8.0$ Hz, *ortho*-H), 7.32–7.39 (m, 3H, *meta*- and *para*-H); protons of PPh_3 ligand: 7.713 (ddd, 6H, $^3J_{HH} = 7.7$, $^4J_{HH} = 1.8$, $^3J_{HP} = 11.3$, *ortho*-H), 7.38–7.46 (m, 9H, *meta*- and *para*-H).

2.7. Chloro{2-[2,2-dimethyl-1-(methylamino)propyl]-phenyl-C,N}(triphenylphosphine-P)palladium(II) (6)

Triphenylphosphine (0.0231 g, 0.088 mmol) was added to a suspension of a pure *ortho*-palladated regioisomer **1a** (0.0281 g, 0.044 mmol) in benzene (5 ml). After the reaction mixture was stirred for 50 min at ambient temperature, it was evaporated in vacuo to dryness and the residue was purified using flash-chromatography on 'dry column' [16] (*h* 1 cm, *d* 2 cm; ether–hexane mixtures in ratios from 1:2 up to 5:1 as eluents) to give a chromatographically pure regioisomer **6** in the yield of 97% (0.0496 g, 0.085 mmol). After recrystallization from benzene–hexane the solvated adduct **6**·C_6H_6 was isolated in the yield of 91% (0.0463 g, 0.0797 mmol); m.p. 212–214°C (dec.), R_f 0.42 (ether–hexane 5:1 mixture). Anal. Calc. for $C_{36}H_{39}ClNPPd$: C, 65.66; H, 5.97; N, 2.12. Found: C, 65.26; H, 5.61; N, 2.60%. Recrystallization from CH_2Cl_2–hexane and drying in vacuo (10^{-2} mmHg) affords desolvated complex **6**; m.p. 197–199°C (dec.).

For desolvated **6** adduct: Anal. Calc. for $C_{30}H_{33}ClNPPd$: C, 62.08; H, 5.73; N, 2.41. Found: C, 62.02; H, 5.79; N, 2.16%. ^{1}H-NMR: δ 1.309 (s, 9H, ^{t}Bu), 2.933 (dd, 3H, $^3J_{HCNH} = 6.0$, $^4J_{HP} = 2.4$, NMe), 3.546 (d, 1H, $^4J_{HP} = 6.0$, α-CH), 4.030 (br dq, 1H, $^3J_{HNCH} = 6.0$, $^3J_{HP} = 5.5$, NH); aromatic protons: 6.349 (ddd, 1H, $^3J_{HH} = 7.5$, $^4J_{HH} = 1.1$, $J_{HP} = 5.7$, C^6H), 6.434 (ddd, 1H, $^3J_{HH} = 7.5$, $^3J_{HH} = 7.4$, $^4J_{HH} = 1.2$, C^5H), 6.847 (ddd, 1H, $^3J_{HH} = 7.4$, $^3J_{HH} = 7.5$, $^4J_{HH} = 1.1$, C^4H), and 7.038 (dd, 1H, $^3J_{HH} = 7.5$, $^4J_{HH} = 1.2$, C^3H); protons of PPh_3 ligand: 7.38 (m, 6H, *meta*-H), 7.43 (m, 3H, *para*-H), and 7.712 (m, 6H, $^3J_{HP} = 11.5$, *ortho*-H).

2.8. Structure determination and refinement of complexes 6 and 7

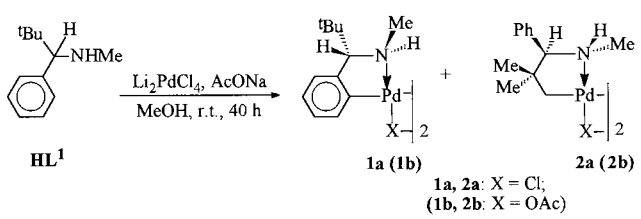
Crystal data, data collection, structure solution and refinement parameters are listed in Table 1. The experimental intensities were corrected for Lorentz and polarization effects [17,18]. All non-hydrogen atoms in both structures were refined in the anisotropic approximation (see Section 6).

3. Results

3.1. Cyclopalladation of secondary amine HL[1]

In our recent paper [15], we described preliminary results for the cyclopalladation of *N*-methyl-α-*tert*-butylbenzylamine (HL^1). In the reaction of secondary amine HL^1 with Li_2PdCl_4 in the presence of AcONa under mild conditions, *ortho*-palladated complex **1a** was isolated in ca. 60% yield as the main product after chromatographic separation from another unidentified complex (Scheme 1); the structure of **1a** was confirmed by spectral investigations of its mononuclear derivatives with PPh_3 and $Acac^-$ [15].

Subsequent more detailed study of this reaction, including ^{1}H-NMR spectra of the reaction mixtures (after chromatographic separation of minor amounts of the diastereomeric coordination complexes *trans*-



Scheme 1.

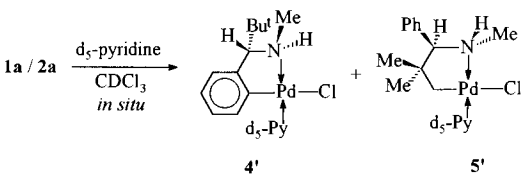
Table 1
Crystal data, data collection, structure solution and refinement parameters for the regioisomeric triphenylphosphine adducts **6** and **7**

Compound	**6**	**7**·$CHCl_3$
Empirical formula	$C_{30}H_{33}ClNPPd$	$C_{30}H_{33}ClNPPd{\cdot}CHCl_3$
Formula weight	580.39	699.76
Color, habit	Light-yellow, block	Colorless, needle
Crystal size (mm)	$0.3\times0.3\times0.1$	$0.38\times0.09\times0.08$
Crystal system	Monoclinic	Monoclinic
Space group	$P2_1/n$	$P2_1/c$
Unit cell dimensions		
a (Å)	10.362(5)	10.9086(2)
b (Å)	13.912(7)	14.4927(3)
c (Å)	18.946(5)	19.7235(2)
β (°)	103.61(4)	90.475(1)
Volume (Å^3)	2655(2)	3118.08(9)
Z	4	4
D_{calc} (g cm^{-3})	1.452	1.491
Absorption coefficient (mm^{-1})	0.879	1.011
$F(000)$	1192	1424
Diffractometer	Enraf–Nonius CAD-4	Siemens SMART CCD
Temperature (K)	293	150.0(2)
Radiation (λ, Å)	Graphite monochromatized Mo–K_α (0.71073)	Graphite monochromatized Mo–K_α (0.71073)
Scan mode	ω	ω
θ Range (°)	2.06–24.98	1.74–26.00
Index ranges (°)	$-12\le h\le11,\ 0\le k\le16,\ 0\le l\le22$	$-12\le h\le14,\ -18\le k\le18,\ -25\le l\le25$
No. reflections collected	4260	19545
No. independent reflections	4143 [$R_{int}=0.0252$]	6124 [$R_{int}=0.0978$]
Data reduction	XCAD4 [17]	Siemens SAINT [18]
Solution method	Direct methods (SHELX-86) [19]	Direct methods (SHELX-86) [19]
Refinement method	Full-matrix least-squares on F^2 (SHELX-93) [20]	Full-matrix least-squares on F^2 (SHELX-93) [20]
Hydrogen treatment	All H atoms were placed in calculated positions and refined using a riding model	All H atoms were found from difference Fourier synthesis and refined with fixed $B_{iso}=0.045$ Å^2
Data/restraints/parameters	4143/0/312	5383/0/446
Goodness-of-fit on F^2	0.984	1.119
Final R indices [$I>2\sigma(I)$]	$R_1=0.0306,\ wR_2=0.0712$	$R_1=0.0607,\ wR_2=0.1079$
R indices (all data)	$R_1=0.0588,\ wR_2=0.0795$	$R_1=0.1064,\ wR_2=0.1378$
Extinction coefficient	0.0000(2)	0.0001(2)
Largest difference peak and hole (e Å^{-3})	0.725 and −0.306	1.758 and −0.917

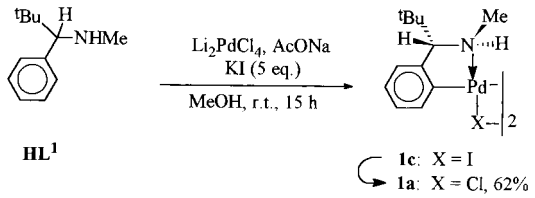
$[Pd(HL^1)_2Cl_2]$ (**3**)) has allowed us to identify the other product as the regioisomeric cyclopalladated complex **2a** formed due to the C–H bond activation of methyl group of the α-*tert*-Bu-substituent in the HL^1 ligand. Taking into account high ability of dimer **1a** to chiral recognition [21], the elaboration of the route of its regioselective formation was very important for its further practical applications.

To provide the ^{1}H-NMR spectral control for the regioselectivity of cyclopalladation under different conditions, the spectra of the regioisomeric dimer **1a/2a** mixture were recorded in $CDCl_3$ containing several drops of d_5-pyridine; under these conditions the mixture of the corresponding mononuclear d_5-Py adducts (**4′/5′**) is actually formed (Scheme 2). Their spectral differentiation was based on the ^{1}H-NMR characteristics of the isolated pyridine adduct of one of two regioisomeric dimers, namely, that of *ortho*-palladated complex **1a** (see below). The spectral characteristics of two regioisomeric d_5-pyridine derivatives are different enough to be used for the reaction course control.

In an attempt to increase the regioselectivity of HL^1 cyclopalladation we modified the conditions of this reaction varying the palladation agent and solvent nature, and temperature regime (see Table 2).



Scheme 2.



Scheme 3.

The using of a rather weak palladation agent (Li_2PdCl_4) in the presence of a standard base (AcONa) under mild conditions (MeOH, r.t., 40 h), results in the formation of two regioisomeric dimeric complexes, **1a** and **2a**, in ca. 2:1 ratio in the total yield of 86% (run 1, see Table 2). When the same reaction was conducted in 1:1 aqueous MeOH (run 2), the ratio of regioisomeric complexes **1a**/**2a** increased up to ca. 4.5:1 (with decrease of the total yield down to 65%). The intermediate regioisomer **1b**/**2b** ratios of 3:1 and 4:1 and total yields of 60–70% were obtained when the palladation of HL^1 was performed with $Pd(OAc)_2$ in glacial AcOH at 60°C and in boiling toluene, respectively (runs 5 and 6).

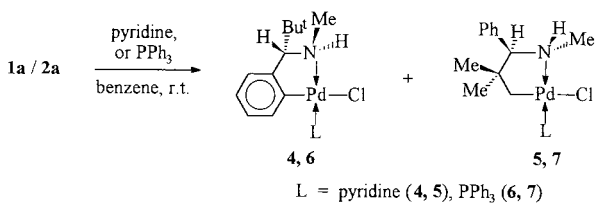
Only for two reaction systems the regioselective *ortho*-palladation of the secondary amine HL^1 was observed. Its reaction with $PdCl_2$ in HMPA at elevated temperature (110–115°C, run 4) results in the formation of only *ortho*-palladated complex **1a**, but in a very low yield of ca. 30%. It seems reasonably to suggest, that this result is due to decomposition of (sp^3)-regioisomer **2a** under high-temperature conditions rather than a consequence of higher regioselectivity.

Finally, the only way to avoid the tedious procedure of regioisomeric complexes separation is the use of PdI_4^{2-} (generated in situ from $PdCl_4^{2-}$ and the excess of I^- ions) as a palladation reagent. The amine HL^1 cyclopalladation by this modified reagent in the presence of AcONa in anhydrous MeOH at room temperature results in regioselective formation of *ortho*-palladated complex $[\{L^1Pd(\mu\text{-}I)\}_2]$ (**1c**), isolated in the acceptable yield of 62% as μ-chloro dimer **1a** after the standard metathesis reactions (run 3, Scheme 3).

As evidence of the crucial role of the secondary nitrogen donor atom for the (sp^3)C–H bond activation, we mention the regioselective *ortho*-palladation of a tertiary amine closely related to HL^1, namely, *N*,*N*-dimethyl-α-*tert*-butylbenzylamine (HL^2) [22]. In the reaction of Li_2PdCl_4 with racemic amine HL^2 in the presence of AcONa in MeOH at a lower temperature (0°C), the corresponding *ortho*-palladated complex was isolated as the sole regioisomer in a rather high yield of 81%. In spite of the conditions used that are the most suitable for the (sp^3)C–H bond activation in the secondary amine HL^1, no signs of *tert*-Bu group palladation in the case of tertiary amine HL^2 were found.

3.2. Mononuclear derivatives of regioisomeric complexes: preparation and separation

Unfortunately, due to the close chromatographic mobility of two regioisomeric dimers **1a** and **2a** (R_f 0.71 and 0.76, respectively, in the optimal solvent system, see Section 2), the isolation of minor component **2a** becomes a very difficult problem. After three-fold column chromatography, along with a pure (sp^2)-regioisomer **1a**, only a sample enriched in an (sp^3)-regioisomer **2a** was obtained (up to an 80:20 ratio of **2a**/**1a**). A regioisomerically pure dimer **1a** thus obtained was used for the preparation of undoubted samples of its mononuclear derivatives.



Scheme 4.

Table 2
Regioselectivity of HL^1 cyclopalladation

Run	Reaction conditions					Regioisomer **1a**/**2a** ratio	Yield (%) [d]
	Reagent	Base	Solvent	*T* (°C)	Time (h)		
1	Li_2PdCl_4	AcONa	MeOH	25	40	2:1	86
2	Li_2PdCl_4	AcONa	MeOH–H_2O (1:1)	25	48	4.5:1	65
3	Li_2PdI_4 [a]	AcONa	MeOH	25	15	>98:2 [b]	62
4	$PdCl_2$	none	HMPA	60, 110–115	2, 2	>98:2	30
5	$Pd(OAc)_2$	none	AcOH	60	4	3:1 [c]	60
6	$Pd(OAc)_2$	none	benzene, toluene	60, 110	2, 1.5	4:1 [c]	70

[a] Generated in situ by treatment of Li_2PdCl_4 with ca. five equivalents of KI.
[b] μ-Iodo dimer **1c** was transformed into the μ-chloro dimer **1a** by treatment with $AgNO_3$ and then LiCl.
[c] After conversion of the mixture of μ-acetato dimers **1b**/**2b** into the μ-chloro dimers **1a**/**2a** by metathesis with LiCl.
[d] Total yield of two regioisomeric complexes after chromatographic purification of their mixture without isomers separation.

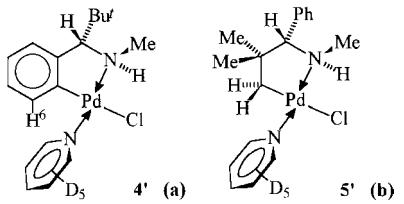


Fig. 1. Illustration of the shielding effects for the C^6H proton of phenylene ring in *ortho*-palladated adduct **4′** (a) and of one of $PdCH_2$ protons in the case of its (sp^3)-regioisomer **5′** (b).

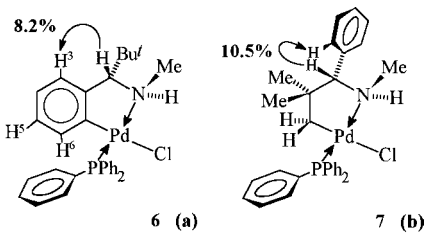


Fig. 2. Illustration of the shielding effects for the C^6H proton of the phenylene ring in *ortho*-palladated adduct **6** (a) and of one of $PdCH_2$ protons in the case of its (sp^3)-regioisomer **7** (b), and selected $^1H\{^1H\}$ NOE values for both regioisomeric phosphane adducts.

Subsequent attempts to separate two regioisomeric palladacycles were made with mononuclear derivatives of dimeric complexes **1a**/**2a**. The mixtures of mononuclear regioisomers were obtained by routine reaction of the μ-chloro bridge cleavage in the corresponding dimers with pyridine or triphenylphosphine to afford the mixtures of **4**/**5** and **6**/**7** adducts, respectively (Scheme 4).

Recrystallization of the mixture of the regioisomeric pyridine derivatives **4**/**5** followed by separation of two kinds of crystals by hand gave a pure *ortho*-palladated complex **4** in the moderate yield of 42%. Taking into account the feasibility of its easy conversion to dimer state via elimination of pyridine ligand (by protonolysis or using column chromatography [23]), this way may be considered as an alternative route to dimer **1a**. As for (sp^3)-complex **5**, it may be obtained by this procedure in the highly regioisomerically enriched state only.

In the case of phosphane adducts **6**/**7**, both regioisomers were isolated in rather low yields by means of multiple recrystallizations of their mixtures from different solvent systems. Thus, chromatographically pure *ortho*-palladated complex **6** was obtained in 24% yield after two-fold recrystallization of the starting mixture from a benzene–heptane mixture (the same complex was prepared from pure *ortho*-palladated dimer **1a**). Subsequent three-fold slow recrystallization of the mother liquor enriched by (sp^3)-regioisomer **7** from the benzene–ether mixture under cooling affords chromatographically and analytically pure complex **7** in 13% yield. Despite rather tedious procedures for regioisomer separation, their isolation in the pure state offers a valuable opportunity to their spectral study directed towards comparative analysis of the conformational features of the two kinds of palladacycles.

3.3. Spectral characterization of regioisomeric complexes

The spectrum of *ortho*-palladated dimer **1a** contains only one set of signals that indicates its existence in solutions as only one of four possible *cis*/*trans* and *meso*/*racemic* isomers. The aromatic protons are presented by three groups of multiplets of the total integral intensity of [4H], i.e. in accordance with the palladation at the phenyl ring. The aromatic C^6H proton nearest to the palladation site is the most deshielded one (δ 7.14 ppm) because of its close proximity to the anisotropy domain of μ-chloro ligands [22,24–26]. A rather pronounced broadening of this resonance ($\Delta\delta_{1/2}$ ca. 30 Hz) may be considered as an indication of the dynamic flexibility of these dimeric particles.

The ^{1}H-NMR spectra of the mononuclear derivatives (**4–7**) are more useful for the distinction between the two possible palladation sites. The spectrum of the d_5-pyridine adduct **5′** contains two singlets for the diastereotopic CMe_2 groups at δ 0.663 and 1.062 ppm; upfield shift ($\Delta\delta$ −0.36 ppm) of the first signal compared to δ 1.02 ppm reported for the related α-nonsubstituted palladacycle [27] allows us to assign it to the *pseudo*-equatorial CMe group, taking into account the preferable equatorial orientation of the α-Ph ring (see Section 3.4). The diastereotopic protons of the CH_2Pd group are presented by AB pattern at δ 1.730 and 2.185 ppm with $^2J_{HH}$ 8.3 Hz. The difference between the chemical shifts of two methylene protons ($\Delta\delta$ 0.46 ppm) caused by the magnetic anisotropy of the pyridine ligand [28] (see Fig. 1(b)) may serve as an evidence for (i) the *trans*-*N*,*N*-geometry of complex, and (ii) a rather puckered conformation of this aliphatic five-membered palladacycle, with (iii) the *quasi*-equatorial position of the PdCH proton revealing the upfield shift to δ 1.730 ppm.

By comparison, the ^{1}H-NMR spectrum of the pyridine adduct of *ortho*-palladated regioisomer **4′** displays a nine-proton singlet for the intact ^{t}Bu group at δ 1.26 ppm and four distinct C^3H–C^6H signals in the aromatic region (δ 7.01–6.19). The consequence of the latter is typical for the related *ortho*-palladated benzylamines [15,22,26,29,30] (see Fig. 1(a)). The signal for the α-CH proton appears as a singlet at δ 3.35 ppm in the spectrum of **4′**, but as a doublet at δ 3.34 ppm ($^3J_{HCNH}$ 11.9 Hz) in the case of regioisomeric complex **5′**; this difference may serve as an indication for different conformations of the two regioisomeric palladacycles.

The ^{1}H-NMR spectra of phosphane adducts **6** and **7** support the structure of regioisomeric palladacycles and *trans*(*N*,*P*)-geometry of these complexes (Fig. 2). In the

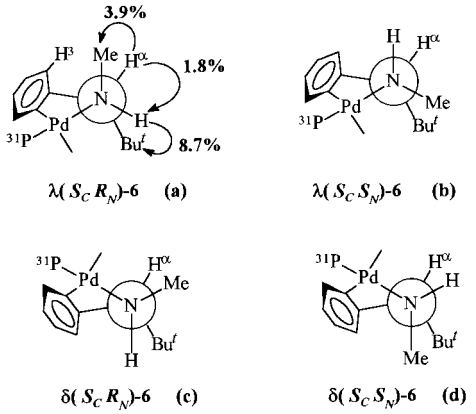


Fig. 3. Newman projections of palladacycles along the N–C(α) bond for the (sp^2)-regioisomer **6** in the (S_CR_N)* ((a), (c)) and (S_CS_N)* relative configuration ((b), (d)) for λ ((a), (b)) and δ conformations ((c), (d)).

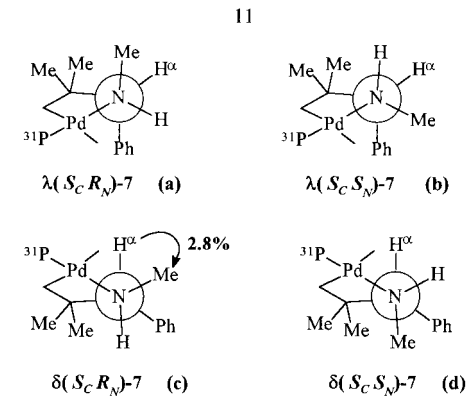


Fig. 4. Newman projections of palladacycle for (sp^3) regioisomer in the (S_CR_N)- ((a), (c)) and (S_CS_N)-configuration ((b), (d)) for λ ((a), (b)) and δ conformations ((c), (d)).

case of (sp^3)-regioisomer **7** the palladation at the *tert*-Bu group is quite evident from the presence of two signals of the diastereotopic CMe groups (singlets at δ 0.578 and 1.015 ppm). Their differentiation was based on a rather strong shielding ($\Delta\delta$ 0.44 ppm) of the *pseudo*-equatorial CMe group (δ 0.578 ppm) by the ring current of the α-Ph substituent (cf. [27]). The diastereotopic $PdCH_2$ protons are presented by the AB part of an ABX system with X = ^{31}P (δ 1.140 and 1.804 ppm). The first signal assignment to the *quasi*-equatorial PdCH proton was deduced from its remarkable high-field shift ($\Delta\delta$ 0.66 ppm) caused by the anisotropy of the aromatic PPh rings of the phosphane ligand, and a very large value of $^1H-^{31}P$ spin–spin coupling constant ($^3J_{HP}$ 9.4 Hz, cf. [27]). The α-Ph group is presented by unresolved multiplet of *meta*- and *para*-protons (δ 7.32–7.39 ppm, [3H]) and double doublet of *ortho*-protons (δ 7.134 ppm, [2H]) that supports the intact state of the phenyl ring. The assignment of the latter signal was supported by its large enhancement (10.5%) under irradiation of the α-methine proton (Fig. 2(b)).

The ^{1}H-NMR spectrum of regioisomer **6** is typical for phosphane adducts of other *ortho*-palladated benzylamines [15,21,26,31] including derivatives of primary [29] and tertiary α-*tert*-Bu substituted benzylamines [22,32]. The intact state of the *tert*-Bu group is evident from the presence of a nine-proton singlet at δ 1.309 ppm. Four well resolved signals of aromatic C^6H-C^3H protons of the palladated phenylene ring reveal an interval of δ 6.35–7.04 ppm in normal sequence from high to low fields (cf. [22,29,32,33]); their assignment was confirmed by NOE differential spectroscopy (Fig. 2(a)).

All these ^{1}H-NMR spectral characteristics may serve as convincing evidence for the palladation sites in mononuclear complexes **4**–**7** (and starting dimers **1a**, **2a**), i.e. the metallation occurs at the *ortho*-position of the phenyl ring in complexes **1a**,**b** and **4**, **6** but at the methyl group of the *tert*-butyl substituent in the case of regioisomeric complexes **2a**,**b** and **5**, **7**.

3.4. The stereochemistry of regioisomeric palladacycles

The comparison of the stereochemistry of the two regioisomeric five-membered palladacycles (phenyl-annelated and pure aliphatic ones) is of interest in the context of successful applications of homochiral α-*tert*-Bu substituted palladacycles of (sp^2)C–Pd type [21,24,32]. It is desirable to clear up two aspects: (i) the relative configurations of the adjacent C*- and N*-stereocenters, and (ii) the conformational features of the two different palladacycles derived from the same secondary amine. These problems were solved using the NOE technique and analysis of the $^1H-^1H$ and $^1H-^{31}P$ spin–spin coupling efficiency for the two regioisomeric phosphane adducts, **6** and **7**. The Newman projections along the N–C(α) bond for four possible stereochemistries of each of two palladacycles (Figs. 3 and 4) were constructed with regard to the flattened conformation of both five-membered palladacycles.

Several arguments may be presented in favor of the preferable existence of the (sp^2)-palladacycle in the λ(S_CR_N) stereochemistry typical for derivatives of other α-alkylbenzylamines [29,32,34,35].

(i) A rather large value of the constant $^4J_{HP}$ = 6.0 Hz found for the α-methine proton points to its *quasi*-equitorial orientation [15,22,26,29,32,36] possible only for the λ conformation (Fig. 3(a) and (b)).

(ii) The absence of any detectable $^1H-^1H$ spin–spin α-C–H/N–H coupling is indicative of roughly orthogonal orientation of these bonds (dihedral angle −86.2° was found from X-ray data for adduct **6** in crystal) in accordance with the Carplus–Conroy equation [37]. Such a geometry may be achieved only in the case of the λ(S_CR_N) stereochemistry (Fig. 3(a)).

(iii) Irradiation of the α-CH proton results in the enhancement of the NMe and NH resonances expectable for both forms of the λ conformation (Fig. 3(a) and (b)). However, the more intense response of the NMe group compared to that of the NH proton (3.9 and 1.8%, respectively, in accordance with the corresponding dihedral angles of +32.9 and −86.2° for crystalline **6**) allows us to choose the $\lambda(S_CR_N)$ configuration as the most reasonable one (Fig. 3(a)).

(iv) The correctness of this conclusion may be also supported by a large enhancement of the signal of the *tert*-Bu protons under irradiation of the NH proton (8.7%). This is impossible in the case of the alternative $\lambda(S_CS_N)$ stereochemistry with their *quasi*-transoid disposition (Fig. 3(b)).

(v) The absence of any influence of the NMe proton irradiation on the signal of the *tert*-Bu protons is in accordance with the $\lambda(S_CR_N)$ stereochemistry of palladacycle in the (sp^2) regioisomer **6**.

The analysis of ^{1}H-NMR spectral data for (sp^3) regioisomeric complex **7** reveals the essential change in the palladacycle conformation. All set of data obtained is compatible with the $\delta(S_CR_N)$ stereochemistry of this aliphatic palladacycle (Fig. 4(c)). This conclusion is deduced from the following data.

(i) The absence of $^1H-^{31}P$ spin–spin coupling for the α-CH proton indicates its *pseudo*-axial position (cf. [26,29,36]). This fact allows us to exclude from consideration the λ conformation of the palladacycle with the *pseudo*-equatorial α-CH proton for both diastereomers (Fig. 4(a) and (b)).

(ii) A rather high-field position of the *ortho*-H signal (δ 7.134 ppm, close to δ 7.17–7.30 ppm for the free ligand HL^1) indicates *quasi*-equatorial disposition of α-Ph substituent in δ conformation (Fig. 4(c) and (d)). To compare, in the case of related α-Ph-substituted benzylaminate palladacycle bearing *quasi*-axial Ph group [33], its *ortho*-protons are considerably deshielded due to the palladium atom anisotropy (δ 7.961 ppm, $\Delta\delta$ 0.58 ppm, cf. [38,39]).

(iii) Irradiation of the α-CH proton results in the marked (3.6%) enhancement of the doublet signal of the *quasi*-axial PdCH proton at δ 1.802 ppm (Fig. 5(a)). This kind of dipolar interaction is impossible for the alternative λ conformation (Fig. 5(b)) independently on the N*-stereocenter configuration. Thus, we can exclude this latter conformation (Fig. 4(a) and (b)) from further considerations.

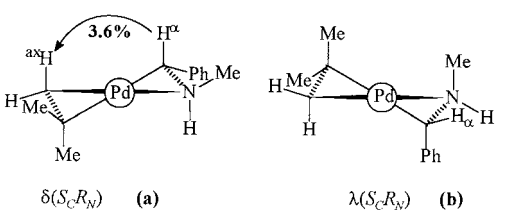


Fig. 5. Projection of the (sp^3) palladacycle along the bisector of the CPdN angle for δ (a) and λ (b) conformations of adduct **7**, illustrating the proximity of α-CH and *quasi*-axial PdCH protons in δ form.

(iv) The choice between two configurations of the most probable δ conformation of palladacycle was based on the marked enhancement of the NMe proton signal (2.8%) under the irradiation of the α-CH proton. The close proximity of these protons is possible only for the $\delta(S_CR_N)$ stereochemistry (Fig. 4(c)), while in the case of the alternative $\delta(S_CS_N)$ configuration they are nearly *trans*-positioned and far removed from each other (Fig. 4(d)).

(v) A high efficiency of the $^1H-^1H$ spin–spin coupling between the α-CH and NH protons provides the most unambiguous evidence of the $\delta(S_CR_N)$ stereochemistry. A very large value of the constant $^3J_{HCNH}$ 12.1 Hz may be explained only by their *transoid* disposition with the torsion angle α-H–C–N–H close to 180° [34,37] (Fig. 4(c)); this angle of 169.9° was found for adduct **7** in crystal state. In all other stereoisomeric forms these bonds are expected to be oriented under angle of ca. 60°.

Thus, the formation of both regioisomeric palladacycles leads to the fixation of the asymmetric nitrogen atom in the configuration opposite to that of the adjacent carbon stereocenter, i.e. (S_CR_N) or (R_CS_N), as it was found previously for other *ortho*-palladated tertiary arylalkylamines [35]. Considerable difference between these two palladacycles is that the δ conformation with *pseudo*-equatorial orientation of the C*-Ph and N*-Me substituents is preferable for the (S_CR_N) configuration in the (sp^3) regioisomer **7** in contrast with the $\lambda(S_CR_N)$ stereochemistry including *pseudo*-axial position of the C*-Bu^t and N*-Me substituents for alternative (sp^2) regioisomer **6**.

3.5. Molecular structure of mononuclear phosphane adducts **6** and **7**

Racemic complexes **6** and **7** crystallize in the monoclinic space groups $P2_1/n$ and $P2_1/c$, respectively, with two pairs of enantiomeric molecules of (S_CR_N) and (R_CS_N) configuration in the unit cell. The crystal of (sp^3)-regioisomer **7** contains the solvate molecule of chloroform. The general view of these regioisomeric complexes and atom numbering schemes is presented in Figs. 6 and 7, respectively; the selected bond lengths and angles are listed in the Tables 3 and 4.

The *ortho*-palladated structure of adduct **6** and cyclopalladation at the *tert*-Bu group in the case of regioisomeric complex **7** are quite evident. As expected from the NMR spectral data, the PPh_3 ligand in both adducts is located *trans* to the nitrogen atom of palladated benzylamine ligand HL^1. Both the complexes have a square planar coordination at palladium atom with tetrahedral distortion more pronounced in the structure

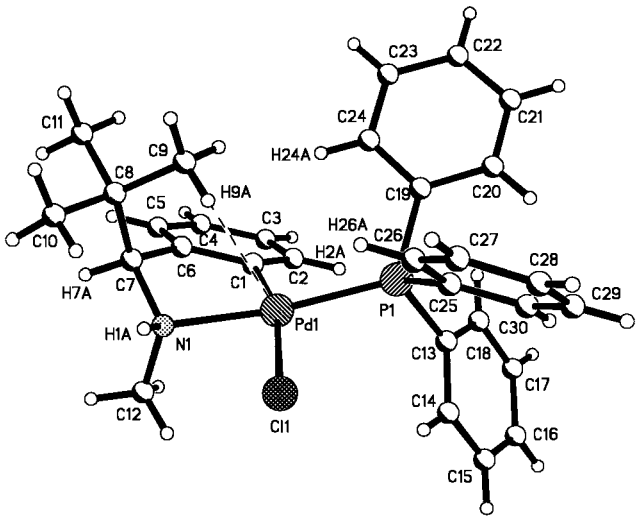


Fig. 6. Molecular structure of the (sp^2)-regioisomeric triphenylphosphine adduct **6**.

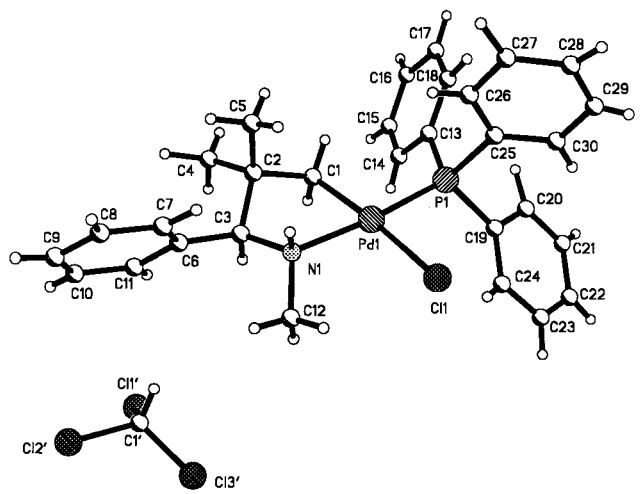


Fig. 7. Molecular structure of the (sp^3)-regioisomeric triphenylphosphine adduct **7**, chloroform solvate.

of *ortho*-palladated complex **6** compared to that for (sp^3)-regioisomer **7**, with the angles between the planes {$NPdC^1$} and {PPdCl} equal to 9.7 and 2.0°, respectively. Almost strictly square-planar coordination seems to be the common property of pure aliphatic five-membered palladacycles (1.9–3.0° [40,41]) while for the phosphane adducts of *ortho*-palladated benzylamines these values are more widely varied (2.4–19.3° [29,32,42,43]).

The Pd–C bond lengths for complexes **6** and **7**, 2.000(4) and 2.046(6) Å, respectively, fall in the ranges 1.99–2.05 [29,32,42–45] and 2.00–2.03 Å [40,41] reported for related phosphane adducts. The Pd–N bond length in the *ortho*-palladated complex **6**, 2.097(3) Å, is intermediate between the values 2.14–2.19 and 2.087–2.092 Å typical for phosphane derivatives of tertiary [32,42,44,45] and primary benzylamines [29,43,46], respectively. In the case of (sp^3) regioisomer **7**, this bond is elongated up to 2.142(5) Å (compared with 2.076–2.086 Å for related cyclopalladated propylamines [40,41]). The Pd–P bond length in both regioisomeric complexes **6** and **7** has the normal values of 2.2549(14) and 2.257(2) Å, respectively (cf. [29,43,45,46]). The Pd–Cl bond in (sp^3) regioisomer **7** is weakened at some extent compared to that in (sp^2) adduct **6** (2.445(2) and

Table 3
Selected bond lengths (Å) and bond angles (°) for the (sp^2)-regioisomeric triphenylphosphine adduct **6**

Bond lengths			
Pd(1)–C(1)	2.000(4)	C(8)–C(10)	1.533(6)
Pd(1)–N(1)	2.097(3)	C(13)–C(14)	1.377(5)
Pd(1)–P(1)	2.2549(14)	C(13)–C(18)	1.386(6)
Pd(1)–Cl(1)	2.3854(12)	C(14)–C(15)	1.376(6)
P(1)–C(13)	1.820(4)	C(15)–C(16)	1.377(8)
P(1)–C(25)	1.824(4)	C(16)–C(17)	1.361(7)
P(1)–C(19)	1.828(4)	C(17)–C(18)	1.386(6)
N(1)–C(12)	1.471(5)	C(19)–C(24)	1.380(5)
N(1)–C(7)	1.495(5)	C(19)–C(20)	1.395(5)
C(1)–C(2)	1.398(6)	C(20)–C(21)	1.384(6)
C(1)–C(6)	1.410(5)	C(21)–C(22)	1.356(6)
C(2)–C(3)	1.379(6)	C(22)–C(23)	1.362(6)
C(3)–C(4)	1.362(6)	C(23)–C(24)	1.393(5)
C(4)–C(5)	1.391(6)	C(25)–C(30)	1.389(5)
C(5)–C(6)	1.383(5)	C(25)–C(26)	1.401(6)
C(6)–C(7)	1.506(6)	C(26)–C(27)	1.374(6)
C(7)–C(8)	1.553(6)	C(27)–C(28)	1.376(6)
C(8)–C(9)	1.517(5)	C(28)–C(29)	1.374(7)
C(8)–C(11)	1.528(5)	C(29)–C(30)	1.373(6)
Bond angles			
C(1)–Pd(1)–N(1)	80.0(2)	C(9)–C(8)–C(10)	109.3(4)
C(1)–Pd(1)–P(1)	96.66(12)	C(11)–C(8)–C(10)	107.8(4)
N(1)–Pd(1)–P(1)	173.29(9)	C(9)–C(8)–C(7)	113.8(3)
C(1)–Pd(1)–Cl(1)	164.41(11)	C(11)–C(8)–C(7)	107.8(4)
N(1)–Pd(1)–Cl(1)	86.82(10)	C(10)–C(8)–C(7)	109.6(4)
P(1)–Pd(1)–Cl(1)	97.26(5)	C(14)–C(13)–C(18)	118.8(4)
C(13)–P(1)–C(25)	102.2(2)	C(14)–C(13)–P(1)	117.0(3)
C(13)–P(1)–C(19)	106.5(2)	C(18)–C(13)–P(1)	124.2(3)
C(25)–P(1)–C(19)	100.8(2)	C(13)–C(14)–C(15)	120.7(5)
C(13)–P(1)–Pd(1)	111.83(13)	C(16)–C(15)–C(14)	120.4(5)
C(25)–P(1)–Pd(1)	115.15(13)	C(17)–C(16)–C(15)	119.4(5)
C(19)–P(1)–Pd(1)	118.60(14)	C(16)–C(17)–C(18)	120.8(5)
C(12)–N(1)–C(7)	112.2(3)	C(13)–C(18)–C(17)	120.0(5)
C(12)–N(1)–Pd(1)	112.6(3)	C(24)–C(19)–C(20)	118.0(4)
C(7)–N(1)–Pd(1)	107.6(2)	C(24)–C(19)–P(1)	122.0(3)
C(2)–C(1)–C(6)	117.5(4)	C(20)–C(19)–P(1)	120.0(3)
C(2)–C(1)–Pd(1)	128.8(3)	C(21)–C(20)–C(19)	120.6(4)
C(6)–C(1)–Pd(1)	112.8(3)	C(22)–C(21)–C(20)	120.0(4)
C(3)–C(2)–C(1)	121.1(4)	C(21)–C(22)–C(23)	121.0(4)
C(4)–C(3)–C(2)	121.4(4)	C(22)–C(23)–C(24)	119.5(4)
C(3)–C(4)–C(5)	118.7(4)	C(19)–C(24)–C(23)	120.9(4)
C(6)–C(5)–C(4)	121.1(4)	C(30)–C(25)–C(26)	118.2(4)
C(5)–C(6)–C(1)	120.2(4)	C(30)–C(25)–P(1)	122.7(3)
C(5)–C(6)–C(7)	122.3(4)	C(26)–C(25)–P(1)	119.1(3)
C(1)–C(6)–C(7)	117.2(3)	C(27)–C(26)–C(25)	120.1(4)
N(1)–C(7)–C(6)	104.1(3)	C(26)–C(27)–C(28)	120.9(4)
N(1)–C(7)–C(8)	113.6(3)	C(29)–C(28)–C(27)	119.5(4)
C(6)–C(7)–C(8)	117.6(3)	C(30)–C(29)–C(28)	120.4(4)
C(9)–C(8)–C(11)	108.4(4)	C(29)–C(30)–C(25)	120.9(4)

Table 4
Selected bond lengths (Å) and bond angles (°) for the (sp^3)-regioisomeric triphenylphosphine adduct **7**, chloroform solvate

Bond lengths			
Pd(1)–C(1)	2.046(6)	C(9)–C(10)	1.36(1)
Pd(1)–N(1)	2.142(5)	C(10)–C(11)	1.394(9)
Pd(1)–P(1)	2.257(2)	C(13)–C(18)	1.398(9)
Pd(1)–Cl(1)	2.445(2)	C(13)–C(14)	1.409(9)
P(1)–C(13)	1.827(6)	C(14)–C(15)	1.383(9)
P(1)–C(19)	1.835(6)	C(15)–C(16)	1.39(1)
P(1)–C(25)	1.837(6)	C(16)–C(17)	1.39(1)
Cl(1′)–C(1′)	1.779(8)	C(17)–C(18)	1.399(9)
Cl(2′)–C(1′)	1.729(9)	C(19)–C(24)	1.387(9)
Cl(3′)–C(1′)	1.721(9)	C(19)–C(20)	1.394(9)
N(1)–C(12)	1.476(8)	C(20)–C(21)	1.397(9)
N(1)–C(3)	1.497(7)	C(21)–C(22)	1.38(1)
C(1)–C(2)	1.549(8)	C(22)–C(23)	1.38(1)
C(2)–C(5)	1.535(9)	C(23)–C(24)	1.389(9)
C(2)–C(4)	1.529(8)	C(25)–C(30)	1.383(9)
C(2)–C(3)	1.541(8)	C(25)–C(26)	1.397(9)
C(3)–C(6)	1.515(8)	C(26)–C(27)	1.393(9)
C(6)–C(7)	1.397(9)	C(27)–C(28)	1.38(1)
C(6)–C(11)	1.394(9)	C(28)–C(29)	1.36(1)
C(7)–C(8)	1.393(9)	C(29)–C(30)	1.40(1)
C(8)–C(9)	1.39(1)		
Bond angles			
C(1)–Pd(1)–N(1)	83.0(2)	C(10)–C(9)–C(8)	118.8(7)
C(1)–Pd(1)–P(1)	92.1(2)	C(9)–C(10)–C(11)	121.3(7)
N(1)–Pd(1)–P(1)	174.8(1)	C(10)–C(11)–C(6)	120.7(6)
C(1)–Pd(1)–Cl(1)	173.9(2)	C(18)–C(13)–C(14)	118.7(6)
N(1)–Pd(1)–Cl(1)	90.9(1)	C(18)–C(13)–P(1)	123.2(5)
P(1)–Pd(1)–Cl(1)	93.93(5)	C(14)–C(13)–P(1)	118.0(5)
C(13)–P(1)–C(19)	100.2(3)	C(15)–C(14)–C(13)	120.5(6)
C(13)–P(1)–C(25)	104.8(3)	C(14)–C(15)–C(16)	120.2(7)
C(19)–P(1)–C(25)	103.7(3)	C(17)–C(16)–C(15)	120.4(6)
C(13)–P(1)–Pd(1)	118.9(2)	C(16)–C(17)–C(18)	119.9(6)
C(19)–P(1)–Pd(1)	117.8(2)	C(17)–C(18)–C(13)	120.3(6)
C(25)–P(1)–Pd(1)	109.6(2)	C(24)–C(19)–C(20)	119.6(6)
C(12)–N(1)–C(3)	111.4(5)	C(24)–C(19)–P(1)	119.9(5)
C(12)–N(1)–Pd(1)	115.9(4)	C(20)–C(19)–P(1)	120.4(5)
C(3)–N(1)–Pd(1)	108.8(3)	C(21)–C(20)–C(19)	120.0(7)
C(2)–C(1)–Pd(1)	109.1(4)	C(22)–C(21)–C(20)	120.3(7)
C(5)–C(2)–C(4)	109.3(5)	C(21)–C(22)–C(23)	119.3(7)
C(5)–C(2)–C(3)	111.4(5)	C(22)–C(23)–C(24)	121.1(7)
C(4)–C(2)–C(3)	109.7(5)	C(23)–C(24)–C(19)	119.7(6)
C(5)–C(2)–C(1)	111.2(5)	C(30)–C(25)–C(26)	119.0(6)
C(4)–C(2)–C(1)	108.9(5)	C(30)–C(25)–P(1)	122.4(5)
C(3)–C(2)–C(1)	106.2(5)	C(26)–C(25)–P(1)	118.5(5)
N(1)–C(3)–C(6)	113.9(5)	C(27)–C(26)–C(25)	120.7(7)
N(1)–C(3)–C(2)	108.2(4)	C(28)–C(27)–C(26)	118.8(7)
C(6)–C(3)–C(2)	116.0(5)	C(29)–C(28)–C(27)	121.0(7)
C(7)–C(6)–C(11)	117.8(6)	C(28)–C(29)–C(30)	120.7(7)
C(7)–C(6)–C(3)	123.0(5)	C(25)–C(30)–C(29)	119.8(7)
C(11)–C(6)–C(3)	119.2(6)	Cl(3′)–C(1′)–Cl(2′)	113.2(5)
C(6)–C(7)–C(8)	120.8(6)	Cl(3′)–C(1′)–Cl(1′)	110.5(5)
C(9)–C(8)–C(7)	120.6(7)	Cl(2′)–C(1′)–Cl(1′)	110.4(4)

2.3854(12) Å, respectively) as the consequence of stronger *trans*-influence of the alkyl–Pd bond compared to that of aryl–Pd.

The stereochemistry of both palladacycles is in complete agreement with the predictions derived from ^{1}H-NMR data: it is $\lambda(S_CR_N)$ in the case of *ortho*-palladated adduct **6** but $\delta(S_CR_N)$ for its (sp^3)-regioisomeric counterpart **7**. The five-membered palladacycle in *ortho*-palladated complex **6** has the twisted envelope-like conformation (bent along the α-C···Pd line is of 43.8°). In accordance with the $\lambda(S_CR_N)$ configuration of the palladacycle in **6**, α-*tert*-Bu and NMe substituents at the adjacent C* and N* stereocenters are nearly *trans*-oriented in *quasi*-axial positions with the α-C–CMe_3 bond deviated from the normal to the mean coordination plane by only 6.6°.

In the case of the (sp^3) regioisomer **7** the palladacycle twist is more pronounced compared to **6**: the averaged magnitudes of the absolute values of intrachelate dihedral angles equal 33.2 and 26.9°, respectively. In accordance with the δ conformation of the (sp^3) palladacycle in **7**, α-Ph and NMe substituents at the adjacent C* and N* stereocenters adopt *quasi*-equatorial orientation, with deviation of C^3–C^6 and N–C^{12} bonds from the normal to the mean coordination plane of 101.0 and 52.0°, respectively. It should be mentioned an almost ideal transoid disposition of α-H–C and N–H bonds with the torsion angle α-H–C–N–H equal to 169.9° that is in line with the ^{1}H-NMR data ($^3J_{HCNH}$ 12.1 Hz).

The most remarkable structural peculiarity of *ortho*-palladated complex **6** is a rather close approach of one of hydrogen atoms of *tert*-Bu group to the palladium center: Pd···H^{9a}(Bu^t) distance of 2.705 Å is noticeably shorter than the sum of van der Waals radii of these atoms (3.1 Å [47]) and, probably, corresponds to some kind of secondary interaction (cf. [29]). Such *tert*-Bu···Pd interaction may contribute to some extent to the stabilization of the $\lambda(S_CR_N)$ or δ (R_CS_N) conformation of palladacycles with axially-oriented bulky substituents.

4. Discussion

The fact that intramolecular palladation of secondary amine HL[1] occurs for a non-activated ^{t}Bu group is not too surprising. Currently, a number of examples of intramolecular C–H bond activation of Me groups belonging to the *tert*-butyl, neopentyl or pivaloyl substituent in some heterocyclic compounds, such as 2-neopentylpyridine [48], 2-pivaloylpyridine [28], 6-*tert*-butyl-2,2′-dipyridine [25,49], 1-*tert*-butylpyrazol (HL^3) [50,51], 2-*tert*-butylbenzothiazol (HL^4) [52] and 2-*tert*-butyloxazoline [53], are known. All of these cyclopalladated complexes contain five- or six-membered palladacycles with a heterocyclic imine nitrogen donor center. Cyclopalladated derivatives of tertiary *N*,*N*-dimethylneopentylamine [27] are the most closely related models of our (sp^3) regioisomeric complexes reported here.

However, it should be kept in mind that all of the above-mentioned ligands contain the *tert*-Bu group as

the sole possible site of palladation. In all cases $Pd(OAc)_2$ was used as the metallation agent (in C_6H_6 or AcOH at temperatures of 50–100°C); the yield of cyclopalladated complexes was generally not more than 30–40%. Also, attempts to achieve activation of the (sp^3)C–H bond in HL^3 and HL^4 ligands using Na_2PdCl_4 were unsuccessful: instead of cyclopalladated complexes, only mono- or binuclear coordination compounds with monodentate ligands, *trans*-$[Pd(HL^3)_2Cl_2]$ [50] or *trans*-$[\{(HL^4)ClPd(\mu\text{-}Cl)\}_2]$ [52], respectively, were isolated. The sole case of the *tert*-Bu group palladation with Na_2PdCl_4 under mild conditions (AcONa, MeOH, r.t., 3 days) have been reported for the reaction of pinacoline oxime [2], which has no alternative metallation sites.

By contrast, cyclopalladation of the secondary amine HL^1 through the activation of the (sp^3)C–H bond (α-*tert*-Bu group) takes place in spite of the competition with the *ortho*-palladation through the activation of the (sp^2)C–H bond (Ph ring of the same ligand). Both processes result in the formation of equally favorable five-membered palladacycles; the (sp^2)C–H bond activation being usually considered as the more preferable process [54].

Furthermore, the activation of the (sp^3)C–H bond in HL^1 ligand was achieved when using a weak palladation agent, Li_2PdCl_4 under mild conditions (room temperature), whereas, the more electrophilic reagent $Pd(OAc)_2$ was used in the most known cases of the *tert*-Bu group activation [27,28,48,50,52]. However, another example of faster metallation of the aliphatic C–H bond in a chloride complex than in the more electrophilic analogue is known: the cyclopalladation of the phosphine ligand in the hydride complex *trans*-$[PdH(X)(PBu^t_3)_2]$ is completed in 0.5 h if $X = Cl$, but this process requires 2–3 h in the case of $X = CF_3COO$ [55].

Moreover, HL^1 contains a secondary amino group well known as a very poor heteroatom donor center for intramolecular palladation of α-aralkylamines compared to the tertiary amino group [56]. To our knowledge, the result presented here is the first case of intramolecular (sp^3)C–H bond activation in the above-mentioned circumstances.

At first glance, the trends observed for the regioselectivity of HL^1 palladation depending on the conditions used (Table 2) do not appear to be consistent with known ones for other alternative sp^3/sp^2 systems. Thus, $PdCl_2$ activates the aromatic C–H bond of *N*-thiobenzoylpyrrolidine (HL^5) in MeOH, but it attacks (sp^3)C–H bond of this ligand in HMPA [6]; cyclopalladation of *N*-methyl-8-methylquinoline-2-carboxaldimine (HL^6) with $PdCl_4^{2-}$ leads to metallation of the heterocyclic ring, whereas the use of $Pd(OAc)_2$ results in the activation of the 8-Me group [4]. However, the solvent polarity effect in the $HL^5/PdCl_2$ system is based on the increase of the C–H acidity of the α-methylene group adjacent to the thioamide function in HL^5 (such influence is impossible in the case of the HL^1 amine). The change of palladation agent from $Pd(OAc)_2$ to $PdCl_4^{2-}$ in the case of the HL^6 metallation results in attack at the (sp^2)C–H bond instead of the (sp^3)C–H bond as a consequence of the change of the precoordination type (such a forced palladation is impossible in the case of HL^1 ligand).

In the absence of such additional factors in the case of HL^1 palladation, the preferable (sp^2)C–H bond activation by $Pd(OAc)_2$ (**1a**/**2a** ratio of ca. 4:1) may be a consequence of the increased electrophilicity of this reagent compared to that of Li_2PdCl_4 (**1a**/**2a** ratio of ca. 2:1) (cf. [9,57]). Another reason for this difference may be the temperature effect: the temperature 60–110°C was used in the $Pd(OAc)_2$ reactions, but room temperature was sufficient in the experiments with Li_2PdCl_4. It is well known from investigations of intermolecular processes that the low temperature is more favorable for alkane activation [54].

The predominant formation of regioisomer **1a** under all conditions used is in good agreement with the well documented thermodynamic preference of the intermolecular arene activation over the alkane activation [54,57]. The observed increase in yield of regioisomer **2a** for the reaction of HL^1 with Li_2PdCl_4 compared to that with $Pd(OAc)_2$ is in accordance with the pseudo-nucleophilic behavior of Pd^{II} in the oxidative addition of the (sp^3)C–H bond [1,58]. When changing from $PdCl_4^{2-}$ to $PdBr_4^{2-}$ and PdI_4^{2-}, further facilitation of this process would be expected. It is known that in intermolecular (sp^3)C–H bond activation the reactivity of $[Pd(HL)_2Hlg_2]$ complexes increases in a sequence $Cl < Br < I$ [57]. However, it is not the case for the HL^1/PdI_4^{2-} system where regioselective formation of *ortho*-palladated complex **1c** was observed. The reasons for this discrepance are unclear to date.

The same reason (insufficient nucleophility of the Pd^{II} center) may be responsible for the lacking of the (sp^3)C–H bond activation product in the case of a tertiary amine related to HL^1, namely, *N*,*N*-dimethyl-α-*tert*-butylbenzylamine (HL^2) [22]. The secondary amino group of the HL^1 ligand is apparently more tightly bound with Pd^{II}: for example, the formation constant for amine complexes $[(dmpe)Pd(Me)L']^+$ [dmpe = 1,2-bis(dimethylphosphino)ethane] increases from 2.4×10^{-5} for $L' = Et_3N$ to 1.0 for $L' = Et_2NH$ [59]. As good evidence of strong coordination of a secondary amino group to palladium(II), we note the observation of chromatographic separation of diastereomeric coordination complexes (S_CS_N,S_CS_N)- (**8a**) and (S_CS_N,S_CR_N)-*trans*-$[Pd(HL^7)_2Cl_2]$ (**8b**), differing in the absolute configuration of N*-stereocenter of chiral ligand, (S_C)-*N*-methyl-α-methylbenzylamine (HL^7) [60]. Their structures and absolute configurations were confirmed by a

single crystal X-ray diffraction [61]. Moreover, it was shown [60] that the isomerization of individual diastereomers **8a** and **8b** (and of some analogous complexes) occurs only after boiling in toluene.

As the result of the weaker coordination of tertiary amine HL^2 (compared to that of HL^1 ligand), the nucleophility of Pd^{II} center must be reduced to some extent, and thus oxidative addition of the (sp^3)C–H bond becomes less favorable. Similar dependence of the aliphatic palladation efficiency on the nucleophilicity of the ligand *N*-donor atom was reported for ketone hydrazones [9].

5. Conclusion

Intramolecular palladation of the (sp^3)C–H bond of the *tert*-butyl group in the *N*-methyl-α-phenylneopentylamine can be achieved in competition with the (sp^2)C–H bond activation where both possible reactions result in the formation of the equally favorable five-membered palladacycles. The activation of the (sp^3)C–H bond occurs with $PdCl_4^{2-}$ with assistance of the secondary amino group as the directing hetero-donor center in the benzylamine ligand. Regioselective activation of the (sp^2)C–H bond was achieved with PdI_4^{2-} as the palladation agent. In the case of related tertiary *N*,*N*-dimethyl-α-*tert*-butylbenzylamine, *ortho*-palladation is the sole process observed.

The most essential stereochemical difference between two regioisomeric palladacycles is the opposite chirality of their conformations: the $\lambda(S_CR_N)$ stereochemistry is achieved in the case of *ortho*-palladated complexes while the $\delta(S_CR_N)$ conformation is preferable for its (sp^3)-regioisomeric counterpart both in solution and in crystal.

6. Supplementary material

Crystallographic data (excluding structure factors) for the structures reported in this paper have been deposited with the Cambridge Crystallographic Data Centre as supplementary publication nos. CCDC-138517 and -138518. Copies of the data can be obtained free of charge on application to CCDC, 12 Union Road, Cambridge CB2 1EZ, UK (fax: int. code + 44-1223-336033; e-mail: deposit@ccdc.cam.ac.uk).

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