Cyclopalladation of (*S*)-4-*tert*-Butyl-2-methyl-2-oxazoline: An Unprecedented Case of (sp^3)C−H Bond Activation Resulting in *exo*-Palladacycle Formation

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Direct cyclopalladation of (*S*)-4-*tert*-butyl-2-methyl-2-oxazoline at the nonactivated *tert*-butyl group using palladium(II) acetate in acetic acid afforded the first example of an oxazoline-derived *exo*-palladacycle with an (sp^3)C−Pd bond. The structure of the new palladacycle was established using spectroscopic and X-ray studies of the μ-chloro-dimeric complex **2** and two mononuclear triphenylphosphane derivatives: neutral adduct **4** and its cationic benzonitrile-phosphane analogue **5**. Analysis of NMR data for compounds **4** and **5** suggests a highly puckered $\lambda(S)$ conformation of the palladacycle in solution. The X-ray crystal structure of cationic complex **5** confirmed the same highly puckered $\lambda(S)$ conformation of the palladacycle in the solid state; in addition, it revealed unusual $\pi-\pi$-interactions between the phenyl rings of the benzonitrile and PPh_3 ligands and a distorted *M*-propeller configuration of the PPh_3 fragment.

Introduction

The importance of cyclopalladated compounds (CPCs) cannot be overstressed, based on the numerous articles published each year on the subject.[1] Their applications are diverse and have been the subject of reviews[2,3] and numerous papers.[4] One of the most abundant classes of CPCs contains a *CN*-type metallacycle. Many such *CN*-complexes are derived from imines and other C=N bond-containing compounds, including oxazolines. On the basis of the position of the C=N bond relative to the palladacycle, CPCs can have either *endo*- or *exo*-metallacycles (Chart 1). The vast majority of known imine-derived CPCs contain *endo*-palladacycles with the C=N bond being *endo*-cyclic. This preference of C=N bond-containing ligands for the formation of *endo*-palladacycles is so strong that it has been referred to as the "*endo* effect".[5,6] *exo*-Cyclopalladation of imines can be achieved only when *endo*-metalation is impossible[6−9] or strongly disfavored[10] for electronic or steric reasons. Thus far, there has been only one example of an oxazoline-derived *exo*-CPC; this metallacycle (**A**, Chart

Chart 1. General Structures of *endo*- and *exo*-Palladacycles

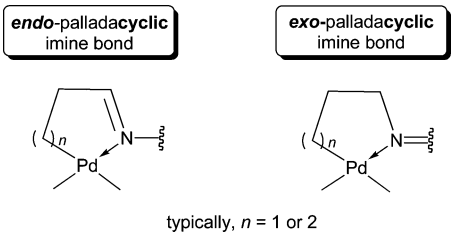

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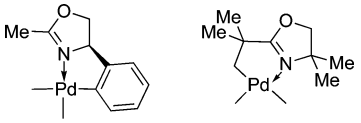
Chart 2. Structures of Palladacycles A and B



A **B**

2) was formed as the result of the (sp^2)C−H activation in (*R*)-2-methyl-4-phenyl-2-oxazoline.[7]

Most cyclopalladated compounds are formed via C−H bond activation at an aryl sp^2- or benzylic sp^3-hybridized carbon. Nevertheless, there are known CPC structures that are formed by C−H bond activation at an aliphatic sp^3-hybrid carbon. Particularly, palladation via *tert*-butyl (sp^3)C−H activation has been reported for phosphane ligands,[3,11] amines,[12] nitrogen heterocycles,[13] oximes,[14,15] and other ligands.[15,16] Among known cyclopalladated oxazolines,[7,17−23] there has been only one complex (**B**, Chart 2) prepared by metalation via (sp^3)C−H activation; this CPC has the *endo* structure.[18] In our search of the literature, no CPC structures with imine-type ligands, including oxazolines, could be found that arise by direct Pd(II) activation of an (sp^3)C−H bond to form an *exo*-palladacycle.

During our ongoing investigations[7,20,21,23] into the cyclopalladation reactions of 2-oxazolines and applications of their corresponding CPCs, (*S*)-4-*tert*-butyl-2-methyl-2-oxazoline (**1**) was synthesized. In this paper, we report our results of the successful cyclopalladation of compound **1** resulting in the formation of a unique CPC (**2**) containing an *exo*-palladacycle accessed by direct Pd(II) (sp^3)C−H activation.

Experimental Section

General Procedures and Instrumentation. Routine ^{1}H, ^{13}C, and ^{31}P NMR (500, 125, and 202 MHz, respectively), DEPT, COSY, and HSQC spectra were recorded in $CDCl_3$ using TMS as an internal standard or triethyl phosphite as an external standard on a Bruker Avance 500 spectrometer. Spin−spin coupling constants, *J*, are given in Hz. IR spectra were recorded on an ATI Mattson Genesis Series FTIR. Analytical TLC was performed on Whatman precoated 250 μm plates of silica gel (F_{254}). Column chromatography and preparative TLC were carried out using Natland silica gel 60 (230−400 mesh). Melting points were measured on a Laboratory Devices Mel-Temp apparatus and were not corrected. Optical rotation measurements were performed on a Rudolph Autopol III automatic polarimeter using a 1 dm tube at room temperature. The low-resolution EI-mass spectrum of **1** was obtained on a Hewlett-Packard 5890 Series II gas chromatograph with a J&W Scientific gas chromatography column (30 m long, i.d. = 0.25 mm, film = 0.25 μm) and a Hewlett-Packard 5971 Series mass selective detector. The high-resolution ES-mass spectrum of **5** was recorded on a Bruker microTOF mass spectrometer. Elemental analyses were performed by Atlantic Microlabs Inc., Norcross, GA. All reagents were used as received from the supplier (Aldrich Chemical Co., Acros, or Strem), unless otherwise noted. Prior to use, palladium(II) acetate was dissolved in hot benzene and filtered, followed by

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solvent removal in vacuo. Glacial acetic acid (GFS Chemicals, ACS "Superior Reagent" grade) was used as purchased, or EM ACS reagent grade acid was distilled from $KMnO_4$. All other solvents were purified by standard procedures prior to use.[24]

Synthesis of (*S*)-4-*tert*-Butyl-2-methyl-2-oxazoline (1). Compound **1** was synthesized as described earlier.[25] The yield of **1** from 2.7453 g (0.022 mol) of ethyl acetimidate hydrochloride and 2.0706 g (0.0177 mol) of (*S*)-*tert*-leucinol was 1.9740 g (79%): R_f 0.38 (1:2 *i*-PrOH−MeCN); bp 153−154 °C (lit. 140−145 °C); IR (neat, ν, cm^{-1}) 1681 (C=N); $[\alpha]_D$ −103°, $[\alpha]_{633}$ −85°, $[\alpha]_{435}$ −208°, $[\alpha]_{546}$ −121° (*c* 0.23, THF); ^1H NMR (δ, ppm) 0.89 (s, 9H, *t*-Bu), 1.98 (d, 3H, $^5J_{HH}$ = 1.4, CH_3C=N), 3.82 (m, 1H, NCH), 4.01 (dd, 1H, $^3J_{OCHR,NCH}$ = 7.8, $^2J_{H^R,H^S}$ = 8.6, OCH^R), 4.15 (dd, 1H, $^2J_{H^R,H^S}$ = 8.6, $^3J_{OCH^S,NCH}$ = 10.1, OCH^S); ^{13}C NMR (δ, ppm) 13.9 (CH_3C=N), 25.8 (*t*-Bu), 68.6 (OCH_2), 76.0 (N*C*H), 164.3 (OCN); EI-MS, *m/z* 141 (M^+), 126 ($M^+ - CH_3$), 96, 85, 56.

Synthesis of (*S,S*)-Di-*μ*-chlorobis{[2-(2-methyl)oxazolin-4-yl]-2,2-dimethylethyl-*C,N*}dipalladium(II) (2). Compound **1** (206.3 mg, 1.461 mmol) was dissolved in 20 mL of glacial acetic acid. $Pd(OAc)_2$ (484.1 mg, 2.156 mmol) was then added to the stirred solution of oxazoline **1**. The reaction mixture was stirred at 80−88 °C for 50 h. The solvent was removed on a rotary evaporator; LiCl (127.8 mg, 3.015 mmol) and anhydrous acetone (30 mL) were added, and the resulting solution was stirred overnight at room temperature. After solvent removal in vacuo, the dark brown crude product was suspended in 1:2 hexanes−CH_2Cl_2 and purified by flash chromatography (SiO_2, d = 4 cm, h = 18.5 cm) using gradient elution (1:2 hexanes−CH_2Cl_2, 1:5 hexanes−CH_2Cl_2, 10:50:1 hexanes−CH_2Cl_2−EtOAc, 5:25:1 hexanes−CH_2Cl_2−EtOAc, and 1:5 EtOAc−CH_2Cl_2). The yield of pure complex **2** was 112.2 mg. A second column was done to purify fractions not adequately separated by the first chromatographic column. The second separation was done using a Biotage "Flash 12i" chromatographic system equipped with a prepacked 12 × 150 mm SiO_2 column. Elution was done using 1:1 hexanes−CH_2Cl_2. The yield of pure complex **2** from the second column was 63.1 mg; the total yield of pure product was 175.3 mg (43%): mp 172 °C (dec); R_f 0.46 (1:20 EtOAc−CH_2Cl_2); $[\alpha]_D$ −201.8°; $[\alpha]_{546}$ −247.7°; $[\alpha]_{633}$ −174.3°; $[\alpha]_{435}$ −555.1° (*c* 0.022, CH_2Cl_2); IR (Nujol, ν, cm^{-1}) 1658 (C=N); ^1H NMR (δ, ppm) 0.84 and 0.91 [two s, 6H, $C(CH_3)_2$], 2.18 (three overlapping signals, 5H, CH_3C=N and $PdCH_2$), 3.98 (m, 2H, OCH_2), 4.27 (m, 1H, NCH); ^{13}C NMR (δ, ppm) 13.6 (H_3CCO), 21.3 and 23.1 [$C(CH_3)_2$], 40.9 (CH_2Pd), 41.3 [$C(CH_3)_2$], 68.6 (OCH_2), 79.4 (NCH), 169.6 (OCN). Anal. Calcd for $C_{16}H_{28}Cl_2N_2O_2Pd_2$: C, 34.06; H, 5.00; N, 4.97. Found: C, 33.81; H, 5.05; N, 4.77.

Synthesis of Dichlorobis[(*S*)-4-*tert*-butyl-2-methyl-2-oxazoline]palladium(II) (3). $PdCl_2$ (32.1 mg, 0.181 mmol) and (*S*)-4-*tert*-butyl-2-methyl-2-oxazoline (54.5 mg, 0.386 mmol) were dissolved in 10 mL of anhydrous methanol. The solution was stirred overnight, and then the solvent was removed in vacuo. The crude product was purified using dry-column vacuum chromatography[26] with gradient elution (SiO_2; h = 0.5, d = 2.5 cm). The yield of purified product was 48.2 mg (58%): mp 185−190 °C (dec); R_f 0.42 (1:9 EtOAc−PhMe); $[\alpha]_{435}$ 1062°; $[\alpha]_{546}$ 372°; $[\alpha]_D$ 289°; $[\alpha]_{633}$ 224° (*c* 0.20, CH_2Cl_2); IR (Nujol, ν, cm^{-1}) 1649 (C=N); ^1H NMR (δ, ppm) 1.33 (s, 9H, *t*-Bu), 2.65 (s, 3H, CH_3C=N), 4.09 (m, 1H, NCH), 4.30 (m, 2H, OCH_2); ^{13}C NMR (δ, ppm) 16.3 (H_3CC=N), 26.4 ($C(CH_3)_2$), 34.0 ($C(CH_3)_2$), 70.1 (OCH_2), 74.0 (NCH), 170.4 (OCN); Anal. Calcd for $C_{16}H_{30}Cl_2N_2O_2Pd$: C, 41.80; H, 6.58; N, 6.09. Found: C, 41.93; H, 6.70; N, 6.00.

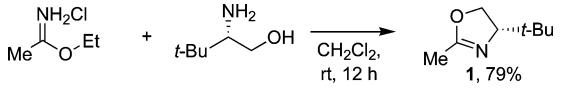
Synthesis of Chloro{[2-(2-methyl)oxazolin-4-yl]-2,2-dimethylethyl-*C,N*}(triphenylphosphane)palladium(II) (4). Triphenylphosphane (83.8 mg, 0.319 mmol) was added to a solution of **2** (89.8 mg, 0.160 mmol) in benzene (15 mL). The mixture was stirred for 1 h at room temperature. Then the solvent was removed in vacuo, and the crude product was purified by trituration with hexanes and filtered. Yield of pale yellow powder was 164.5 mg (95%): R_f 0.27 (1:20 EtOAc−CH_2Cl_2); mp 163−165 °C; $[\alpha]_{546}$ −70°; $[\alpha]_{589}$ −60°; $[\alpha]_{633}$ −51°; $[\alpha]_{435}^{22}$ −121° (*c* 0.08, CH_2Cl_2); IR (thin film, ν, cm^{-1}) 1651 (C=N); ^1H NMR (δ, ppm) 0.71 (s, 3H, CH_3^R), 0.84 (d, 3H, $^5J_{HP}$ = 0.6, CH_3^S), 1.00 (dd, 1H, $^2J_{HH}$ = 9.9, J_{HP} = 8.6, $PdCH^S$), 1.54 (br d, 1H, $^2J_{HH}$ = 9.9, $PdCH^R$), 2.56 (s, 3H, CH_3C=N), 4.01 (m, 2H, OCH_2), 4.27 (m, 1H, NCH), 7.40 (m, 9H, *m*- and *p*-H of PPh_3), 7.70 (m, 6H, *o*-H of PPh_3); ^{13}C NMR (δ, ppm) 14.0 (CH_3C=N), 21.8 and 25.4 [$C(CH_3)_2$], 41.4 [$C(CH_3)_2$], 46.8 (CH_2-Pd), 68.2 (OCH_2), 78.4 (NCH), 128.0 (d, $^4J_{CP}$ = 10.6, *m*-CH of PPh_3), 130.2 (d, $^5J_{CP}$ = 2.1, *p*-CH of PPh_3), 131.4 (d, $^1J_{CP}$ = 49.8, *ipso*-C of PPh_3), 134.8 (d, $^3J_{CP}$ = 11.5, *o*-CH of PPh_3), 186.0 (C=N); ^{31}P NMR (δ, ppm) 35.5 (PPh_3). Anal. Calcd for $C_{26}H_{29}ClNOPPd$: C, 57.37; H, 5.37; N, 2.57. Found: C, 57.36; H, 5.47; N, 2.44.

Synthesis of (Benzonitrile){[2-(2-methyl)oxazolin-4-yl]-2,2-dimethylethyl-*C,N*}(triphenylphosphane)palladium(II) Tetrafluoroborate (5). A solution of benzonitrile (6.9 mg, 0.067 mmol) in anhydrous dichloromethane (0.65 mL) was added to compound **4** (34.0 mg, 0.062 mmol), which dissolved with stirring to give a light yellow solution. $AgBF_4$ (16.4 mg, 0.084 mmol) suspended in anhydrous nitromethane (2 mL) was added to the stirred solution of compound **4**, and a colorless precipitate (AgCl) appeared immediately. The reaction flask was flushed with nitrogen, capped with a $CaCl_2$ tube, and covered with a dark cloth to exclude light; the reaction proceeded for 3.5 h with stirring at room temperature in the dark. The product solution was diluted to twice its volume with dry dichloromethane and filtered. The solvent was removed from the filtrate on a rotary evaporator (rt water bath), and the oily residue was then dried under high vacuum for 3 h to give a colorless foamy solid. The crude product was purified by crystallization from nitromethane containing a trace of benzonitrile and diethyl ether as cosolvent. Yield: 31.1 mg (72%) of clear, colorless crystals; mp 168−170 °C; $[\alpha]_D$ −20.5°, $[\alpha]_{633}$ −15.5°, $[\alpha]_{435}$ −34.7°, $[\alpha]_{546}$ −17.6° (*c* 0.196); IR (thin film,ν, cm^{-1}) 1646 (C=N), 2258 (C≡N); ^1H NMR ($CDCl_3$, δ, ppm) 0.78 (s, 3H, CH_3^R), 0.92 (s, 3H, CH_3^S), 1.41 (t, 1H, $^2J_{HH} \approx J_{HP} \approx$ 10.1, $PdCH^S$), 1.73 (br d, 1H, $PdCH^R$), 2.31 (s, 3H, H_3CC=N), 4.09 and 4.13 (2 overlapping t, 2H, $^2J \approx {}^3J_{OCH^R,NCH} \approx$ 8.4, OCH^R and NCH, respectively), 4.48 (br t, 1H, $^2J \approx$ 8.4, $^3J_{OCH^S,NCH} \approx$ 10.4, OCH^S), 7.30 (m, 2H, *m*-H of PhCN), 7.48 (m, 11H, *m*- and *p*-H of Ph_3P and *o*-H of PhCN), 7.63 (m, 7H, *o*-H of Ph_3P and *p*-H of PhCN); ^{13}C NMR ($CDCl_3$, δ, ppm) 13.9 (H_3CC=N), 21.9 (CH_3^S), 24.8 (CH_3^R), 42.2 [$C(CH_3)_2$], 46.6 (CH_2-Pd), 69.1 (OCH_2), 77.8 (NCH), 109.1 (*ipso*-C of PhCN), 121.3 (C≡N), 129.0 (d, $^3J_{CP}$ = 11.0, *m*-CH of Ph_3P), 129.2 (d, $^1J_{CP}$ = 38.6, *ipso*-C of Ph_3P), 129.5 (*m*-CH of PhCN), 131.4 (d, $^4J_{CP}$ = 2.3, *p*-CH of Ph_3P), 132.6 (*o*-CH of PhCN), 134.2 (d, $^2J_{CP}$ = 11.8, *o*-CH of Ph_3P), 134.7 (*p*-C of PhCN), 170.7 (d, $^3J_{CP}$ = 5.8, H_3CC=N); ^{31}P NMR (CD_2Cl_2, δ, ppm) 36.3 (PPh_3). Anal. Calcd for $C_{33}H_{34}BF_4N_2OPPd$: C, 56.72; H, 4.90; N, 4.01. Found: C, 56.21; H, 4.76; N, 4.03.

X-ray Crystallographic Analysis of 5. Single crystals of **5** suitable for X-ray diffraction analysis were grown by slow diffusion of hexane vapor into a toluene solution at −20 °C. A colorless, block crystal of dimensions ca. 0.38 × 0.32 × 0.24 mm was mounted onto a 0.1 mm diameter glass capillary. Data collection was done using a Bruker SMART Platform CCD diffractometer at 173(2) K;[27] the θ range used for data collection was 1.68−27.55°. The intensity data were corrected for absorption and decay using an empirical correction for absorption anisotropy.[28] The structure of **5** was solved and

(24) Armarego, W. L. F.; Perrin, D. D. *Purification of Laboratory Chemicals*, 4th ed.; Butterworth Heinemann: Oxford, UK, 2002.
(25) Meyers, A. I.; Shipman, M. *J. Org. Chem.* **1991**, *56*, 7098.
(26) Pedersen, D. S.; Rosenbohm, C. *Synthesis* **2001**, 2431.
(27) *SMART* V5.054 ed.; Bruker Analytical X-ray Systems: Madison, WI, 2001.

Scheme 1



refined using SHELXS-97 software.[29] Systematic absences and intensity statistics were used to determine the space-group as $P2_12_12_1$. A direct-methods approach provided the locations of most non-hydrogen atoms from the electron density map; however, full-matrix least-squares/difference Fourier cycles were used to locate the remaining non-hydrogen atoms. Hydrogens were placed in ideal positions and were refined as riding atoms with relative isotropic displacement parameters. Chirality was established by anomalous dispersion effects in the diffraction data.

Crystallographic data for **5** has been deposited with the Cambridge Crystallographic Data Centre as supplementary publications no. CCDC-262111. Copies of the data can be obtained free of charge on application to CCDC, 12 Union Road, Cambridge CB2 1EZ, UK [fax: int. code + 44(1223)-336-033; e-mail: deposit@ccdc.cam.ac.uk].

Results and Discussion

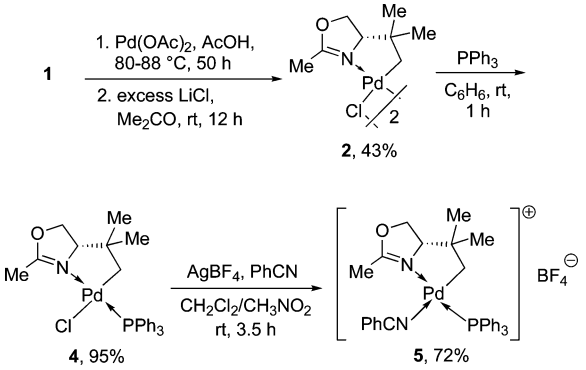
Direct Palladation of (*S*)-4-*tert*-Butyl-2-methyl-2-oxazoline (1). Compound **1** was synthesized by cyclization of the corresponding imidate hydrochloride and (*S*)-*tert*-leucinol using a procedure previously reported for this compound (Scheme 1).[25]

Two aspects of oxazoline **1** offer significant challenges to cyclopalladation. First, its structure permits only formation of an *exo*-type palladacycle (see Introduction). In addition, the aliphatic (sp^3)C−H bond that must be acted upon by palladium is not activated by any adjacent functional groups. As one would expect based on these limitations, a series of initial attempts met with little success.

Diverse combinations of palladation agent, solvent, base, and temperature regime were tested in reactions with oxazoline **1**, including the mild reagent $Na_2[PdCl_4]$, cationic reagent $[Pd(NCMe)_4](BF_4)_2$,[30] (in MeCN or THF, in the presence of K_2CO_3, Cs_2CO_3, or Ag_2CO_3 for both palladating agents), and the very electrophilic complex $Pd(CF_3CO_2)_2$ (in TFA at room temperature or 65 °C, in the presence of CF_3CO_2Na or without it). However, no desired CPCs were detected under these conditions (TLC and ^{1}H NMR data). In the case of $Pd(CF_3CO_2)_2$, formation of Pd(0) was observed along with complete oxazoline **1** decomposition. In the reactions of compound **1** (HL) with $[Pd(NCMe)_4](BF_4)_2$ and $Na_2[PdCl_4]$, only coordination complex $[Pd(HL)_2Cl_2]$ (**3**) was isolated (21−79%). The same result was obtained in attempts to employ a solid-phase reaction of **1** with $Pd(OAc)_2$: only coordination complex **3** was observed in the resulting mixture (TLC and ^{1}H NMR data).

Success in cyclopalladation of compound **1** has been achieved only using $Pd(OAc)_2$ as the palladation agent

Scheme 2



in acetic acid solution. The desired CPC **2** was isolated in the reaction of $Pd(OAc)_2$ with **1** in the presence of AcONa (with metal−oxazoline−base 1:1:1−5 ratios) in acetic acid at 60−75 °C, followed by treatment with LiCl. The low yields of the dimer **2** (typically 6−18%) using these conditions prompted us to seek some routes to improve this method. The reactant stoichiometry was not found to exert a significant influence on palladation efficiency: the yield of dimer **2** remained constant (ca. 23%) in two reactions performed with metal−oxazoline 2:1 and 1:2 ratios. Surprisingly, the experimental workup was found to make a significant impact on the product yield. In our previous studies,[7,20,21,23] inorganic impurities were removed from the crude product by simple aqueous extraction; however, removing this step and using only chromatographic purification gave a substantial increase in yield of the desired CPC **2** (to 35%).

Reactions using $Pd(OAc)_2$ as the palladation reagent generated a large amount of Pd(0), especially if the reaction temperature was not carefully maintained under 90 °C. It was found, however, that the extent of palladium reduction could be somewhat decreased by exclusion of the base NaOAc from the reaction mixture. Contrary to our findings for another 2-oxazoline,[20] the product yield was increased to 43% when NaOAc was eliminated from the reaction mixture and no aqueous workup was done (Scheme 2).

In all reactions of compound **1** (HL) with $Pd(OAc)_2$, a significant amount (20−50%) of the coordination complex $Pd(HL)_2Cl_2$ (**3**) was found. For comparison, this complex was also obtained in a yield of 58% by reacting $PdCl_2$ with oxazoline **1** in a ratio of 1:2 in methanol.

It is noteworthy that dimeric complex **2** is soluble not only in $CHCl_3$ and CH_2Cl_2 but also in acetone and benzene. A similar *exo*-dimer derived from (*R*)-2-methyl-4-phenyl-2-oxazoline is only sparingly soluble in $CHCl_3$ and CH_2Cl_2. For comparison, the μ-Cl dimer of *endo*-cyclopalladated (*S*)-4-*tert*-butyl-2-phenyl-2-oxazoline is highly soluble in $CHCl_3$, but the corresponding complex of 2-phenyl-2-oxazoline is practically insoluble in this solvent. The same trend has been observed for analogous complexes of benzylamines: their solubility in $CHCl_3$ depends on the number and the size of alkyl groups. It has been found that an increase in the size and number of alkyl groups in the ligand increases the solubility of the corresponding μ-Cl dimers in $CHCl_3$.

For subsequent characterization studies, dimeric CPC **2** was converted to its mononuclear PPh_3 adduct (**4**;

(28) Blessing, R. *Acta Crystallogr. A* **1995**, *51*, 33.
(29) *SHELXS-97*, V6.14 ed.; Bruker Analytical X-ray Systems: Madison, WI, 2000.
(30) (a) van Manen, H.-J.; Nakashima, K.; Shinkai, S.; Kooijman, H.; Spek, A. L.; van Veggel, F. C. J. M.; Reinhoudt, D. N. *Eur. J. Inorg. Chem.* **2000**, 2533. (b) Murahashi, T.; Nagai, T.; Okuno, T.; Matsutani, T.; Kurosawa, H. *Chem. Commun. (Cambridge)* **2000**, 1689. (c) Huck, W. T. S.; van Veggel, F. C. J. M.; Kropman, B. L.; Blank, D. H. A.; Keim, E. G.; Smithers, M. M. A.; Reinhoudt, D. N. *J. Am. Chem. Soc.* **1995**, *117*, 8293. (d) Sen, A.; Lai, T.-W. *J. Am. Chem. Soc.* **1981**, *103*, 4627.

Scheme 2). Complex **4** was further transformed into an ionic benzonitrile complex using $AgBF_4$ (**5**; Scheme 2).

Spectral Characterization of Complexes. Spectral characterization of the obtained complexes (**2**−**5**) was done using NMR (^{1}H, ^{13}C, ^{31}P, DEPT, HSQC, and COSY) and IR spectroscopy. Complex **5** was analyzed by NOESY spectra as well.

Metalation at the *tert*-butyl group of oxazoline **1** becomes quite evident from comparison of the ^{1}H NMR spectra of compound **1** and coordination compound **3** with spectra of cyclometalated complexes **2**, **4**, and **5.** The nine-proton singlet of the *tert*-butyl group in the spectra of oxazoline **1** and the monodentate *N*-bonded oxazoline moiety in coordination complex **3** (near δ 0.9 and 1.3 ppm, respectively) is replaced in the spectra of compounds **2**, **4**, and **5** by signals for two diastereotopic methyl groups (**2**, **4**, and **5**) and two signals from the diastereotopic palladium-bonded methylene protons (**4** and **5**). Unfortunately, in the case of dimer **2** signals resulting from the diastereotopic $PdCH_2$ protons were not well resolved in $CDCl_3$ or C_6D_6 solutions. These signals, as well as the signal of the methyl group located at the 2-position of the oxazoline ring, were overlapped to give a multiplet at ca. δ 2.2 ppm with integral intensity corresponding to five protons. However, the HSQC spectrum clearly showed that the multiplet at ca. 2.2 ppm belongs to the protons attached to two different carbons. Furthermore, the DEPT135 spectrum indicated that protons having a signal at δ 2.2 ppm correlated to a methylene carbon.

In the IR spectra of complexes **2**−**5**, the C=N stretching frequencies were shifted to lower wavenumbers ($\Delta\nu$ = 23−35 cm^{-1}) compared to that of compound **1** (1681 cm^{-1}). This shift indicated that the imine nitrogen is coordinated to the palladium center.[7,20,21]

Mononuclear complexes **4** and **5** are best suited for further analysis of new palladacycle conformation because they contain phosphorus, which can provide valuable stereochemical data, and have better ^{1}H NMR signal resolution. For both phosphane derivatives, standard *cis*(*P,C*)-geometry of the palladium coordination sphere has to be expected, since carbon has a greater *trans*-influence.[32] This assumption is confirmed by the NOESY spectrum recorded for compound **5**: there were no NOESY cross-peaks observed between the singlet of the oxazoline 2-methyl group (δ 2.31 ppm) and the δ 7.63 ppm multiplet, as would be expected for a putative *trans*(*N,N*),*trans*(*P,C*)-complex. The latter downfield multiplet has to be considered as the result of overlapping of signals from the *ortho* hydrogens of the PPh_3 rings and the *para* hydrogen of the PhCN ligand, on the basis of the COSY spectrum of **5**, the [7H] integral intensity, previously reported data for triphenylphosphane complexes of other cyclopalladated oxazolines,[7,20,21] and known spectral data for free benzonitrile.[33] By contrast, a rather strong cross-peak was found between the same multiplet at δ 7.63 ppm and the singlet at δ 0.92 ppm assigned to one of the two diastereotopic methyl groups of the oxazoline ligand. Considering that for either geometry of the palladium environment in complex **5** the *para* proton of the PhCN ligand will be too far from any palladacycle protons to display NOE enhancement, this effect may be attributed only to phosphane *ortho*-H interaction with one of the CMe_2 groups, which may be evidence of the *cis*(*N,N*)-geometry of this complex. This conclusion was confirmed by X-ray study of complex **5** (vide infra). Similarities in the spectral features (signal chemical shifts in ^{1}H, ^{13}C, and ^{31}P NMR and multiplicities in ^{1}H NMR spectra) for complexes **4** and **5** may be considered as evidence of the PPh_3 ligand position *trans* to the oxazoline nitrogen atom in both compounds. The ^{31}P NMR spectra of **4** and **5** contain one peak, revealing that both complexes exist in solution as only one geometric isomer.

High-resolution mass spectral characterization of complex **5** gave a base peak of m/z = 508.1030, which corresponds to the *C,N*-oxazoline and the triphenylphosphane ligands attached to a palladium (mass accuracy 0.8 ppm). Facile loss of the benzonitrile ligand under rather gentle conditions of the positive ESI method is indicative of its weak coordination with the palladium atom, which may be a consequence of the very strong *trans*-influence of an (sp^3)-carbon.

As reference points for differentiation of diastereotopic protons/groups of the palladacycle we have chosen the protons of the oxazoline ring of known *S* absolute configuration. Assignment of the oxazoline ring signals in ^{1}H and ^{13}C NMR spectra was done using standard analysis of their HSQC and DEPT135 spectra. Due to the presence of a chiral center, oxazoline derivatives with substituents at the 4-position usually display separate ^{1}H NMR signals for each of the three heterocycle hydrogens.[7,20,21] Unfortunately, in the ^{1}H NMR spectra of dimer **2** and its phosphane adduct **4** (measured in $CDCl_3$) the signals of two of three oxazoline hydrogens were overlapped to give two multiplets near δ 4.0 [2H] and 4.3 ppm [1H] corresponding to the OCH_2 and NCH protons of the oxazoline ring, which is in accordance with previously reported values.[7,20,21,23] In the ^{1}H NMR spectrum of cationic complex **5** taken at room temperature in $CDCl_3$, signals of two hydrogens at δ 4.09 and 4.13 ppm are only partly overlapped. The HSQC spectrum proved that the two overlapping triplets at δ 4.13 and 4.09 ppm and the triplet at 4.48 ppm belong to the NCH and diastereotopic OCH_2 hydrogens, respectively.

The NOESY spectrum of complex **5** reveals strong cross-peaks between the multiplet centered at $\delta \sim 4.11$ ppm (resulting from the partial overlap of the NCH signal and the signal of one of the OCH_2 hydrogens) and both singlets at δ 0.78 and 0.92 ppm belonging to the diastereotopic CMe_2 groups. Since efficient interaction may be possible only between protons or groups located in the *cisoid* position relative to the $C^5-C^4-C^\alpha$ plane, these two strong NOE responses can be explained as a result of interactions between the NCH and CMe^R, and the OCH^R and CMe^S, protons (Figure 1).[34] Consequently, the multiplet centered at $\delta \sim 4.11$ ppm has to contain the signal of the OCH^R proton, and as a result,

(31) Compound **1** and $Pd(AcO)_2$ were dissolved in CH_2Cl_2, and silica gel was added. The solvent was then removed on a rotary evaporator; the mixture was stirred for 2 days at 50 °C, then extracted with methanol and treated with LiCl.

(32) Dunina, V. V.; Gorunova, O. N. *Russ. Chem. Rev.* **2005**, *74*, in press.

(33) Pretsch, E.; Bühlmann, P.; Affolter, C. *Structure Determination of Organic Compounds Tables of Spectral Data*, 3rd ed.; Springer: Berlin, 2000.

(34) Here and later *S* and *R* prochiral groups will be depicted as Me^S, H^S, Me^R, H^S, etc.

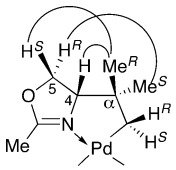


Figure 1. Assignment of diastereotopic methyl groups based on their NOE contacts with the oxazoline ring protons in complex **5**.

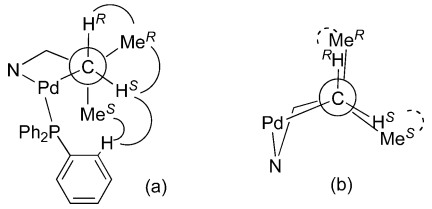


Figure 2. Newman projections of the palladacycle in **5** along the (Pd)CH_2−CMe_2 bond for the actual chiral $\lambda(S)$ conformation with the observed NOE contacts (a) and for the alternative nontwisted envelope with its expected NOE contacts (b).

the triplet at δ 4.48 ppm may be assigned to the OCH^S proton. Since the NOESY spectrum of **5** shows a weak cross-signal between this triplet at δ 4.48 ppm and the singlet at δ 0.78 ppm of the more distant palladacycle's Me group, it provides a basis for assignment of the latter signal to the CMe^R group located in a *cisoid* position to the OCH^S proton. Consequently, the second singlet at δ 0.92 ppm in the spectra of complex **5** may reasonably be assigned to the CMe^S group.

Several arguments can be presented in support of the latter assignment: (i) a molecular model of the *cis*(*N,N*)-isomer of **5** constructed for chiral envelope-like $\lambda(S)$ conformation of the palladacycle showed that the Me^S group of the palladacycle is located in proximity to the *ortho* protons of the PPh_3 ligand (Figure 2a); (ii) X-ray study of **5** (vide infra) revealed a rather short distance of 2.957 Å between a hydrogen of the Me^S group and one of the *ortho*-hydrogens of the PPh_3, while the distances between the Me^R group and *ortho*-hydrogens of two different PPh_3 rings were significantly larger, 4.412 and 5.151 Å; (iii) the aforementioned strong cross-peak between the signal of *ortho*-PhP protons and the singlet at δ 0.92 ppm is in complete accordance with these data; (iv) in the ^1H NMR spectra of another phosphane adduct **4** the similar low-field signal of the CMe_2 group (at δ 0.84 ppm) appears as a doublet ($^5J_{HP}$ 0.6 Hz); such marked $^1H\cdots^{31}P$ spin−spin coupling through five bonds seems to be very unusual and may be partly explained by direct interaction of these nuclei through space. Therefore, high-field signals at δ 0.84 or 0.92 ppm in the ^1H NMR spectra of phosphane adducts **4** and **5**, respectively, may be assigned to the Me^S group of the palladacycle.

Strong NOESY cross-peaks (Figure 2a) observed in the spectra of **5** between the singlet at δ 0.78 ppm corresponding to the Me^R group with both the triplet at δ 1.41 ppm and the doublet at 1.73 ppm resulting from the diastereotopic hydrogens of the $PdCH_2$ fragment provide the best evidence of the palladacycle's chiral envelope-like $\lambda(S)$ conformation (Figure 3). For the alternative achiral (nontwisted) conformation, only one very strong cross-peak would be predicted for each pair, $PdCH^R\cdots Me^R$ and $PdCH^S\cdots Me^S$, located in the

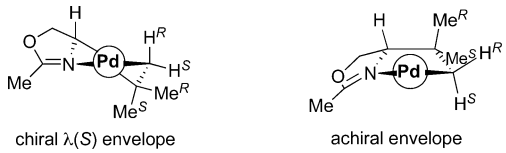


Figure 3. Chiral $\lambda(S)$ (actual) and nontwisted (alternative) envelope conformations of the palladacycle in complex **5**.

eclipsed position (Figure 2b); consequently, this nontwisted conformation (Figure 3) may be excluded from further considerations. The NOE enhancement observed for the triplet at δ 1.41 ppm, due to interactions of the corresponding PdCH hydrogen with the *ortho* hydrogens of the P−Ph rings, allows us to identify this signal as belonging to the $PdCH^S$ proton.

Analysis of the observed signal multiplicities for the $PdCH_2$ fragment in the ^1H NMR spectrum of phosphane derivatives **4** and **5** provides additional evidence in favor of the $\lambda(S)$ conformation of the palladacycle. In this conformation, the $PdCH^R$ hydrogen related to the doublet at δ 1.73 ppm is situated in a pseudo-axial position, and the $PdCH^S$ hydrogen, giving rise to the triplet at δ 1.41 ppm, occupies the pseudo-equatorial position relative to the mean coordination plane. According to the molecular model, the expected torsion angle for the P−Pd−C−H^R fragment should be close to 80−90°, and due to the orthogonality of the P−Pd and C−H^R bonds, efficient spin−spin coupling would not be expected. For this reason, the signal of the $PdCH^R$ proton appeared as a doublet with the geminal coupling constant $^2J_{HH}$ = 10.1 Hz. The appearance of the $PdCH^S$ proton signal as a triplet suggests an advantageous torsion angle for the P−Pd−C−H^S fragment (estimated at 30−40° using a molecular model, found by X-ray crystal structure analysis 34.4°). In addition, the $PdCH^S$ hydrogen is in very close proximity (2.76 Å in the crystal structure) to the phosphorus atom. The observed coupling constant J_{HP} can, therefore, be explained by spin coupling of the two nuclei through three bonds and from through-space interaction. It is noteworthy that the same multiplicity pattern for the $PPdCH_2$ fragment was reported for the phosphane derivative of another aliphatic palladacycle.[35]

The conformation of the oxazoline ring in compound **1** and complex **5** in $CDCl_3$ was assessed on the basis of the values of coupling constants for the oxazoline hydrogens. The values of the torsion angles H−C^4−C^5−H^S and H−C^4−C^5−H^R in compounds **1** and **5** were estimated using the computer program MastRe-J.[36] The program enabled torsion angles for H−C^4−C^5−H^S and H−C^4−C^5−H^R to be calculated using the Haasnoot−de Leeuw−Altona equation relating torsion angle to J. The obtained torsion angle values are provided in Figure 4. The values suggest that the oxazoline ring in both compound **1** and complex **5** has the same slightly twisted $\delta(S)$ conformation. The torsion angle values calculated for complex **5** are in fair agreement with the experimental values (4.4° for the H−C^4−C^5−H^S torsion angle and 125.6° for the H−C^4−C^5−H^R torsion angle) from the X-ray diffraction study of **5**. It is noteworthy

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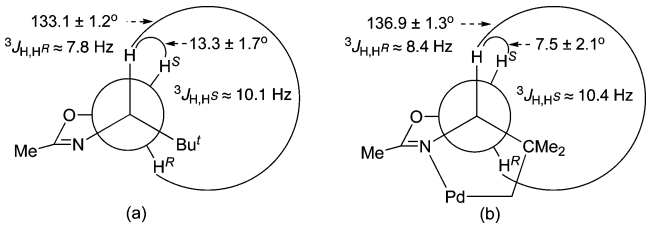

Figure 4. Torsion angle values estimated using the Haasnoot–de Leeuw–Altona equation[36] for the $\delta(S)$ conformation of the oxazoline ring in compound **1** and complex **5**.

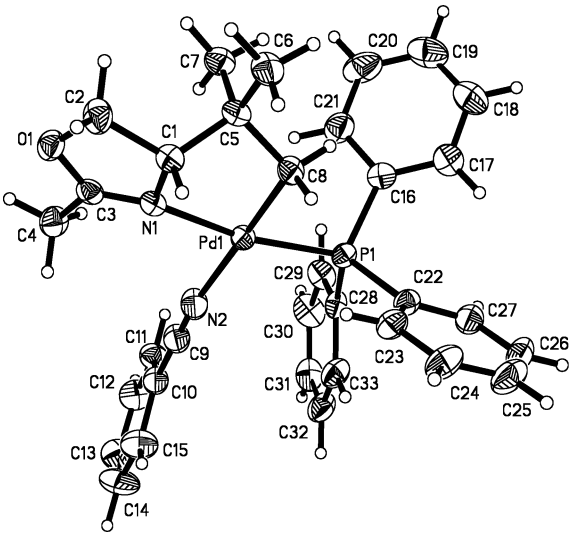

Figure 5. Thermal ellipsoid diagram of the cation of complex **5** showing its numbering scheme. The BF_4 anion is omitted for clarity.

that the $\delta(S)$ conformation of the heterocycle was also suggested on the basis of spectroscopic data for the only known *exo* oxazoline-based palladacycle,[7] while the oxazoline ring in the corresponding *endo* complexes adopts the $\lambda(S)$ conformation.[21]

Molecular Structure of Mononuclear Cationic Phosphane Derivative 5. The most conclusive evidence for the cyclopalladated structure of complexes **2**, **4**, and **5** comes from the X-ray diffraction study of the mononuclear cationic derivative **5**: the site of cyclopalladation at the *tert*-Bu group and *cis*(*N,N*)-geometry of the coordination sphere are unambiguous. Complex **5** crystallizes in the orthorhombic space group $P2_12_12_1$ with four molecules in the unit cell. The anion BF_4^- is well separated from the complex cation: the shortest contact distance (H^{24A} to $F^{1'}$) equal to 2.49 Å exceeds the sum of van der Waals radii of these atoms (2.46 Å[37]). The tetrafluoroborate anion is disordered in the crystal, populating two positions in a ratio of 84:16. The general view of this complex and atom-numbering scheme are presented in Figure 5.

Taking into account that this structure is the first example of a structurally characterized chiral oxazoline-derived CPC with the (sp^3)C–Pd bond, it will be compared with other known complexes including aliphatic palladacycles (Chart 3). Among such structurally characterized analogues, there are two dimers (**6a**[38] and **6b**[39]), five mononuclear compounds (**7a**,[35] **7b**,[40] **7c**,[41] **7d**,[42] and **8**[43]), and one bis-chelated spiro-complex **9**[44] (Chart 3). All these derivatives contain a five-membered *CN*-palladacycle with a primary (**9**), secondary (**7a**), or tertiary (**6a**,**b**, **7b**–**d** and **8**) amino group as the donor fragment. Complex **10** (Chart 3), with a tricyclic structure of the *CNNO*-type containing a *CN*-palladacycle with *exo*-imine *N*-donor group, has been reported as well.[45]

The coordination environment of the palladium atom in cationic complex **5** may be described as square planar with very slight tetrahedral distortion: the angle between the planes $\{N^1PdC^8\}$ and $\{PPdN^2\}$ is equal to 2.9°. It is of note that almost ideal square-planar geometry is a common feature in pure aliphatic five-membered *CN*-palladacycles; the tetrahedral distortion angles in complexes **6a**,**b** and **7b**,**d** fall in the range 1.9–3.1°.[38–40,42] In the cases of **7a** and **9**, the metal exists in a very flattened square-pyramidal environment with a slightly twisted base.[35,44] In comparison, tetrahedral distortions in *ortho*-palladated derivatives of 2-aryloxazolines and benzylamines fall into much larger ranges, 1.7–15.8° and 2.4–19.3°, respectively.[7,22,35] Consequently, aliphatic palladacycles due to their pronounced flexibility allow for retention of a square-planar configuration environment, which is optimal for a d^8-metal center such as Pd(II).

The Pd–C bond length for complex **5**, 2.04 Å, falls in the narrow ranges reported for related CPCs with both (sp^3)C–Pd–Cl (1.97–2.05 Å) and (sp^2)C–Pd–Cl axes (1.99–2.05 Å), despite the expected difference in the *trans*-influence of nitrile and chloride ligands. Although this bond is elongated to some extent in the more related cationic complex **10** with (sp^3)C–Pd–N=*C* axis [2.11 Å] and also in the spiro-complex **9** with (sp^3)C–Pd–(sp^3)*C* axis [2.16 Å], such Pd–C bond weakening may be a consequence of steric strain in the tricyclic *CNNO* system of the first model and strong *trans*-influence of the carbanionic center in the second complex.

The Pd–N^1(oxazoline) bond length in complex **5**, 2.098 Å, is longer than in all known examples of *endo*-type *ortho*-palladated oxazolines (1.886–2.085 Å), but is between the normal values of 2.060–2.062 and 2.142–2.188 Å found for phosphane adducts of *ortho*-palladated oxazolines with an *endo*-C=N bond[20,22] and alkylaminate *CN*-palladacycles (**8**, **7a**),[35,43] respectively. Some elongation of the Pd–N bond in the *exo*-adduct **5** compared to oxazoline-derived *endo*-analogues may be explained as resulting from less efficient palladium bonding with the imino-donor group located in the *exo*-cyclic position, due to the absence of intracyclic conjugation with this double bond. This assumption can be supported by similar values of Pd–N bond length

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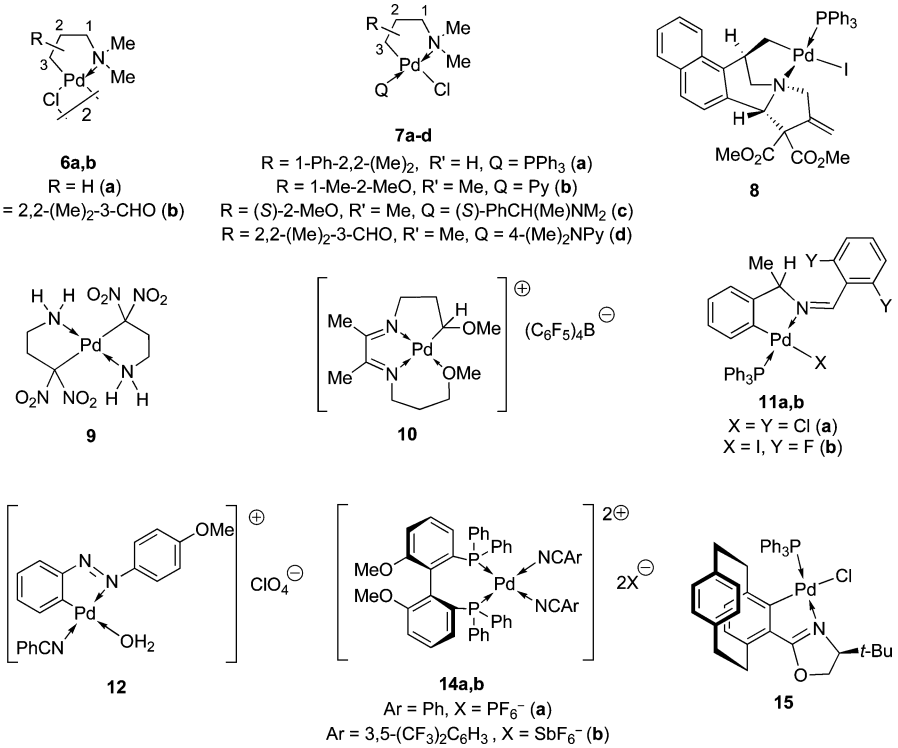
Chart 3. Palladacycles Related to Complex 5 with Reported X-ray Crystal Structures



(2.103−2.112 Å) found for PPh_3 derivatives **11a**,**b** (Chart 3) of *exo*-cyclopalladated imines.[8]

The Pd−P bond length in cationic complex **5**, 2.248 Å, is in good agreement with values (2.243−2.248 Å) reported for neutral *exo*-imine derivatives **11a**,**b**.[8] These values fall within the ranges found previously for the neutral PPh_3 adducts of *ortho*-palladated oxazolines of *endo*-type (2.235−2.256 Å)[21,23] and *ortho*-palladated benzylamines (2.243−2.256 Å).[35,46,47]

The weak coordination of the benzonitrile ligand in complex **5** can be seen from the Pd−N^2 bond length of 2.11 Å. In comparison with the structure of the only known benzonitrile adduct with a *CN*-palladacycle, **12** (Chart 3), the value of the Pd−N(NCPh) bond is 2.01 Å.[48] The Pd−N(NCPh) bond length is further decreased to 1.94−1.99 Å in complexes *trans*-[$PdX_2(NCPh)_2$] [X = Cl (**13a**), Br (**13b**)][49] and in the **13a** component of the crystal Pd_6Cl_{12}·**13a**·*p*-xylene.[49] Such weakening of the Pd−N^2 bond in complex **5** may reasonably be explained as a consequence of the stronger *trans*-influence of the alkyl−Pd bond compared to that of the Pd←N bond.[32] As additional support, it can be mentioned that the Pd−N bond lengths in two reported bis(benzonitrile) diphosphane complexes of the [(P⌒P)Pd($NCPh)_2$] type (**14a**,**b**) vary from 2.06 to 2.12 Å[50] in accordance with the rather large *trans*-influence of the P−Pd bond.[32]

The benzonitrile ligand in complex **5** displays nearly linear coordination to the palladium atom with bond angles Pd^1−N^2−C^9 and N^2−C^9−C^{10} equal to 171.2° and 179.3°, respectively; these values fall in the ranges 170.2−177.1° and 172.9−180.0° found for benzonitrile complexes **12**−**14**. The length of the N^2≡C^9 bond in compound **5** is equal to 1.149 Å, exceeding the value of 1.131 Å reported for analogue **12**, and is close to the upper limit of values found for coordination complexes **13a**,**b** and the crystal Pd_6Cl_{12}·**13a**·*p*-xylene (1.12−1.16 Å).[49]

Another structural peculiarity of complex **5** is the nearly coplanar orientation of the benzonitrile phenyl ring and one of the PPh_3 phenyl rings (A) (Figure 6) characterized by the torsion angle C^8−Pd−P−C^{ipso} of −174.6° and an interplanar angle between these two aromatic rings of 16.5°. Noncovalent attractive interactions between π−π-systems are invoked to account for stabilization and orientation in many systems.[51,52] In recent theoretical studies of intermolecular π−π stacking in simple arene dimers, three geometries are most commonly discussed: sandwich (D_{6h}), parallel-displaced (C_{2h}, "slipped sandwich"), and T-shaped (C_{2v}, "point-to-face").[50−53] In structure **5**, the orientation of the PhCN and P−Ph^A rings resembles the parallel-displaced geometry of two arenes. The closest contact distance between the two aromatic rings is 3.5 Å (C^{10}···C^{32}), which is in accord with experimental values of 3.4−3.6 Å found to be the average interplanar spacing in

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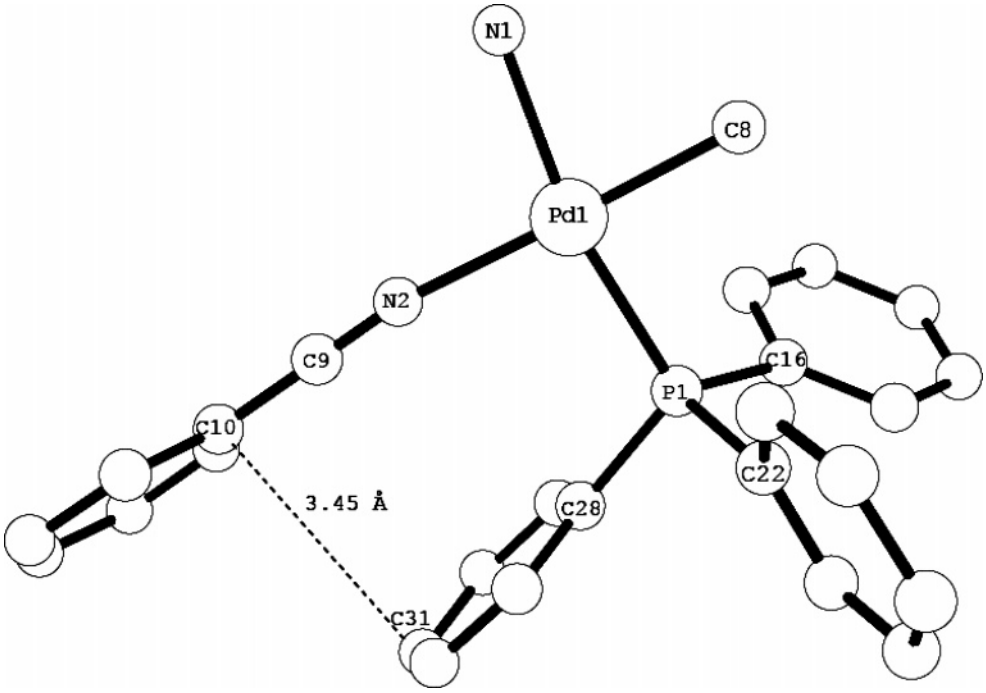

Figure 6. *M* propeller conformation of the PPh_3 ligand in the X-ray structure of complex **5**, which is slightly distorted due to possible $\pi-\pi$ interactions between ring **A** of the PPh_3 fragment and the Ph ring of the benzonitrile ligand (30% probability ellipsoids).

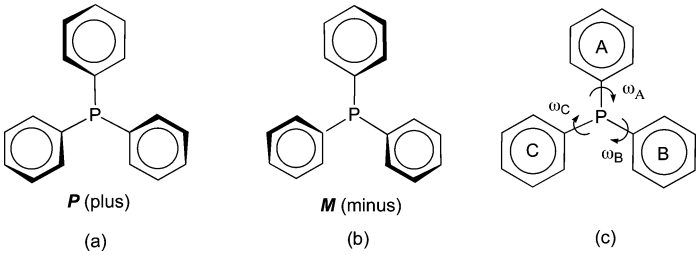

Figure 7. Possible chiral rotameric states *P* (a) and *M* (b), respectively, for the M−PPh_3 moiety derived from achiral C_3-symmetric structures via the Ph-ring rotation around the P−C^{ipso} bonds (c).

porphyrin aggregates.[51] For comparison, a study of substituent effects on $\pi-\pi$ interactions performed by Sinnokrot and Sherrill[52] found a vertical displacement of 3.6−3.8 Å for a sandwich benzene-benzonitrile dimer. Due to the restricted geometry of the arene moieties in **5**, horizontal displacement of the two arenes is 1.39 Å (Figure 6; defined as the distance between the Ph^A-centroid to C^{31}), which is slightly shorter than the calculated horizontal displacements for benzene dimers (1.54−2.10 Å).[52,53] Since the geometric parameters of complex **5** are in good agreement with both theoretical and experimental values for systems with known $\pi-\pi$ interactions, one can reasonably interpret the nearly coplanar orientation of the two arene rings in complex **5** as due to intramolecular $\pi-\pi$ interactions.

The stereochemistry of the coordinated PPh_3 ligand in complex **5** is of special interest since its propeller-like rotameric states can provide additional chirality.[54−56] The Ph_3P−M fragment remains achiral only if all P−Ph rings are positioned either parallel ("parallel" conformation) or orthogonal ("orthogonal" conformation) to the C_3 axis of the PPh_3 moiety (Figure 7).[54] Between the two extremes lie the rotameric states that result from synchronous twisting of the three P−Ph rings (starting from the orthogonal conformation) about the P−C^{ipso} axes.[54] Rotation can be either clockwise or counterclockwise (Figure 7), which generates the chiral propeller-like configurations *P* (*plus*) and *M* (*minus*), respectively. Unfortunately, studies of the influence of other chirality elements on PPh_3 stereochemistry have been mainly restricted to cyclopentadienyl compounds with planar chirality and an asymmetric metal center.[55−57] Recently, a detailed analysis[58] of available X-ray structure data for PPh_3 derivatives of *C**- and *N**-chiral benzylaminate palladacycles has shown that the spirality (helicity) of the phosphane ligand is dependent upon both the palladacycle conformation and the nature of the *N*-donor atom.

The rotameric states of the aromatic rings in the phosphane ligand (relative to the corresponding P−C^{ipso} bonds) in complex **5** were estimated using averaged values of the pair of torsion angles that include the

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ortho-Ph carbons, i.e., Pd−P−C^{ipso}−C^{ortho1} (ω_{i1}) and Pd−P−C^{ipso}−C^{ortho2} (ω_{i2}), according to the known[55] equation $\omega_i = (\omega_{i1} + \omega_{i2} + 180°)/2$. The torsion angle range of 0−90° is indicative of the *P* propeller configuration, while the range 90−180° corresponds to the *M* configuration. For complex **5**, the angles $\omega_A - \omega_B$ are equal to 90.3°, 141.0°, and 177.4° for PPh_3 rings **A** ($C^{ipso} = C^{28}$), **B** ($C^{ipso} = C^{16}$), and **C** ($C^{ipso} = C^{22}$), respectively (Figure 6). These data allow us to describe the PPh_3 conformation as an *M* propeller, distorted due to interaction of ring **A** with the PhCN ligand.

For comparison, the PPh_3 ligands also adopt a helical conformation in related phosphane adducts (S_CR_N)*-**7a** and (*S*)*-**8**, which contain a Pd−CH_2 bond, as well as in the phosphane derivative of the *ortho*-palladated oxazoline (S_C,S_{pl})-**15**[22] (Chart 3). In the structures of these three complexes, two or three values of $\omega_A - \omega_C$ angles (119.6°, 158.5°, and 132.9° for **7a**; 174.0°, 101.7°, and 129.6° for **8**; 85.9°, 138.1°, and 167.8° for **15**) correspond to the *M* propeller configuration of the phosphane ligand. In all reported X-ray data for PPh_3 derivatives of chiral benzylaminate palladacycles,[58] only two PPh rings exist in the twisted state, while the third P−Ph ring adopts a nearly parallel disposition, presumably due to secondary interactions that were not investigated.

The crystal structure of complex **5** has provided valuable information to support the conclusions made from spectral data regarding the geometry of the two phosphane derivatives **4** and **5**. The analysis of the phosphorus atom environment in adduct **5** has revealed its very close proximity to one of two hydrogen atoms in the CH_2Pd fragment, with the H^{8B}···P distance equal to 2.8 Å, which is significantly shorter than the sum of van der Waals radii of these atoms (3.0 Å[37]). This short contact is most likely responsible for efficient through-space $^{31}P\cdots^{1}H$ spin−spin coupling, in addition to through-three-bond interaction, which is also large due to the advantageous H^{8B}−C^8−Pd−P torsion angle of 34.4°. The values of these geometric parameters found in the X-ray crystal structure are in complete accordance with the very large value of the J_{HP} constant (~10.1 Hz) observed for only one of the $PdCH_2$ protons, H^S. The other $PdCH_2$ proton (H^R) is farther from the phosphorus atom [the H^{8A}···P distance equal to 3.27 Å], and its orientation [with the H^{8A}−C^8−Pd−P torsion angle equal to −84.7°] is not suitable for efficient through-bond coupling. For these reasons, no coupling between the phosphorus and the second $PdCH_2$ proton was detected.

Comparable data were obtained for the Pd−CH_2 fragment in related phosphane derivatives **8** and **7a**; the two CH_2···P distances are equal to 3.30 and 2.88 Å for **8** and 3.01 and 3.38 Å for **7a**. An analogous significant difference in the values of two corresponding torsion angles H−C−Pd−P was observed as well: −39.1° and 81.7° for **8** and −40.6° and 83.8° for **7a**. In accordance with these X-ray data, only the pseudo-equatorial proton of the $PdCH_2$ fragment in complex **7a** reveals efficient $^{31}P\cdots^{1}H$ spin−spin coupling, with J_{HP} = 9.4 Hz.[35]

The stereochemistry of the palladacycle in complex **5** is in agreement with the predictions derived from the ^1H NMR data. First of all, the high degree of palladacycle puckering should be mentioned: the average magnitude of the absolute values of intrachelate torsion angles (τ) is equal 34.2°, which is above the range of τ = 28.3−33.2° reported for other related aliphatic *CN*-palladacycles (**6a**,**b** and **7a**−**d**), except the very sterically crowded pentacyclic structure **8** (τ = 37.8°). Such pronounced puckering in the *exo*-palladacycle of compound **5** is in drastic contrast to the rather small extent of nonplanarity found for *endo*-palladacycles derived from oxazolines, which are characterized by the τ range 1.7−10.3° for the majority of such complexes. Only in the case of sterically overcrowded oxazoline-based *endo*-palladacycles with ferrocenylene[19] and paracyclophane[22] frameworks have τ values increased up to 10.4−16.2°.

The palladacycle conformation in complex **5** may be described as a twisted envelope, with the C^α atom at the apex of the flap and a bend of 36.7° along the line N···C^β. Similar conformations, with the C^α or C^β atom at the top of the flap and the corresponding bend of 42.2−48.8°, are typical for the majority of other complexes with aliphatic palladacycle constituents. As might be expected, the most twisting has been observed for the aliphatic carbon chain of the palladacycle in complex **5**, with the greatest values for torsion angles N−C^α−C^β−C^γ and C^α−C^β−C^γ−Pd (−54.9° and 48.3°, respectively). These values fall into the corresponding ranges reported for other complexes of this type (44.8−63.8° and 43.2−48.9°, respectively).

The conformation of the palladacycle in complex **5** may be described as $\lambda(S_C)$ on the basis of the negative sign of torsion angle N−C^α−C^β−C^γ (−54.91°). In accordance with this stereochemistry, one (C^7H_3) of two Me groups of the CMe_2 fragment and the methine hydrogen at the adjacent *C**-stereocenter (C^1H^{1A}) are in strict *trans*-axial positions, with the C^5−C^7H_3 and C^1−H^{1A} bonds deviated from the normal to the mean coordination plane (mcpl) by only 0.13° and 3.87°, respectively. In the $PdCH_2$ fragment, deviations of the C^8−H^{8A} and C^8−H^{8B} bonds from the normal to the mcpl equal 12.13° and 61.98°, respectively, which indicates an axial position for the former and a quasi-equatorial orientation for the latter hydrogen.

Unfortunately, available data do not allow prediction of palladacycle stereochemistry based on the configuration of intracyclic stereocenters. The same type of chirality transfer may be found only for the *CN*-palladacycles bearing one *C**-stereocenter, namely, λ-(S_C)-**5**, (S_C)-**7d***, and $\lambda(S_C)$-**6b***. In the case of polycyclic structures $\delta(R_CR_N)$-**8*** and $\delta(S_C)$-**10*** and palladacycles $\delta(S_CR_N)$-**7a*** and $\lambda(R_CR_C)$-**7b*** bearing several stereocenters, any simple correlation is impossible.

The oxazoline ring in complex **5** adopts a nearly planar conformation, with the average magnitude of the absolute values of intracyclic torsion angles (τ') of 1.5°; this value lies at the low limit of a rather wide range found for the oxazoline-derived CPCs of *endo*-type (τ' 0.4−14.0°).[7,22]

Conclusion

Despite the unfavorable combination of the reduced propensity of (sp^3)C−H bonds to be activated by Pd(II) and disadvantageous *exo*-position of the C=N bond in the target palladacycle, cyclopalladation of (*S*)-4-*tert*-butyl-2-methyl-2-oxazoline was achieved using palladium(II) acetate as metalation agent. This is the first

example of direct cyclopalladation of an oxazoline derivative through the aliphatic group at position 4 of the heterocycle. Spectral investigations of the initial dimeric complex and its mononuclear phosphane derivatives and X-ray diffraction study of an unusual cationic phosphane-benzonitrile derivative confirmed a very high degree of palladacycle puckering and its existence in both the crystal and solution states as the $\lambda(S)$ conformation. This conformation is fixed by the bicyclic structure formed by palladacycle annelation with a chiral oxazoline ring. Peculiarities of the new palladacycle, such as its very pronounced twisting and high conformational stability, create the best conditions for efficient chirality transfer from the carbon stereocenter to other ligands in the palladium environment.

Further research into (sp^3)C−H activation toward formation of optically active CPCs and their applications (estimation of their potential as chirality inductors) is ongoing at this time.

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Supporting Information Available: The crystallographic information file (CIF) for complex **5**. This material is available free of charge via the Internet at http://pubs.acs.org.

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