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Preparation and characterization of cyclopalladated complexes derived from L-(−)-fenchone

Gerard C. Dickmu, Irina P. Smoliakova*

Department of Chemistry, University of North Dakota, 151 Cornell Street, Mail Stop 9024, Grand Forks, ND 58202-9024, USA

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ABSTRACT

L-(−)-Fenchone **4** was reacted with $RONH_2 \cdot HCl$ (R = H or Me) and pyridine in ethanol to give L-fenchone oxime **5a** and the corresponding *O*-methyl derivative **5b** in 64 and 82% yields, respectively. Reactions of oximes **5a**,**b** with $Pd(OAc)_2$ in acetic acid at 80 °C followed by treatment with LiCl provided dimeric cyclopalladated complexes **7a**,**b** in 65 and 49% yields. Compounds **7a**,**b** were then converted to the mononuclear PPh_3 derivatives **8a**,**b** in 99 and 78% yields. The proposed structures of the synthesized complexes were supported by ^1H, $^{13}C\{^1H\}$, DEPT and 2D NMR spectra. Molecular structures of complexes **8a**,**b** confirmed their trans-*N*,*P* geometry and the presence of the (sp^3)C–Pd bond.

Introduction

Numerous applications of optically active cyclopalladated complexes (CPCs) in asymmetric synthesis (e.g., as catalysts or precatalysts [1,2], chiral auxiliaries [3] or reactants [4]) have warranted a search for new types of enantiopure palladacycles, particularly those derived from inexpensive naturally occurring chiral compounds. The most common natural source of chirality in reported enantiopure CPCs is α-amino acids. For example, several groups studied preparation and reactions of (sp^2)*CN*-palladacycles based on derivatives of (*R*)-glycine, L-tyrosine and related α-amino acids [5,6]. There are a number of reports on palladation of optically active oxazolines [7], which are readily obtained from α-amino acids in a few steps [8]. Other naturally occurring optically active compounds, which were used for preparation of palladacycles, include derivatives of (+)-estrone [6] and D-camphor (**1**) [9–11]. For example, *O*-methyloxime [9] and *N*-benzylimine [10] of D-camphor (**2a**,**b**), which are readily synthesized in one step from ketone **1**, undergo (sp^3)C–H bond activation in the presence of $Pd(OAc)_2$ providing unique palladacycles **3a**,**b** (Scheme 1). D-Camphor and many other bicyclic monoterpenoids possess rigid structures that may be an advantageous feature for chiral catalysts; therefore, CPCs based on compounds of this type are important research targets. In this paper, we disclose the preparation and structural characterization of two palladacycles based on another compound from the chiral pool [12], L-(−)-fenchone [**4**, (*R*)-1,3,3-trimethylbicyclo[2.2.1]heptan-2-one].

Results and discussion

Preparation of CPCs based on L-fenchone oximes and their spectral characterization

Readily available and inexpensive L-fenchone (**4**) was converted to two preligands: oxime **5a** and its *O*-methyl derivative **5b** (Scheme 2). To synthesize oxime **5a**, a mixture of L-fenchone, hydroxylamine hydrochloride ($HONH_2 \cdot HCl$) and pyridine was refluxed in EtOH for 48 h [13]. The oxime was isolated in 64% yield. The ^1H and ^{13}C NMR spectra of **5a** contained only one set of signals suggesting that the oxime was in the form of one isomer. When $HONH_2 \cdot HCl$ was replaced with its *O*-methyl analog, oxime **5b** was isolated in 82% yield. The ^{13}C NMR spectrum of **5b** contained two sets of signals; the 94:6 ratio of two geometrical isomers was determined by integration of two MeO signals in the ^1H NMR spectrum.

Cyclopalladation of oximes **5a**,**b** was accomplished using the same reagent and conditions as reported for the preparation of CPC **3b** [9]: $Pd(OAc)_2$, AcOH, 80 °C, 5 h [14]. The dimeric acetato-bridged intermediates **6a**,**b** were converted to their chloro-bridged analogs **7a**,**b** using LiCl in acetone. The latter complexes were reacted with PPh_3 in acetone to form mononuclear derivatives **8a**,**b** (Scheme 3). Chemical composition and purity of complexes **7a**,**b** and **8a**,**b** as

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* Corresponding author. Tel.: +1 701 777 3942; fax: +1 701 777 2331.
E-mail address: irina.smoliakova@email.und.edu (I.P. Smoliakova).

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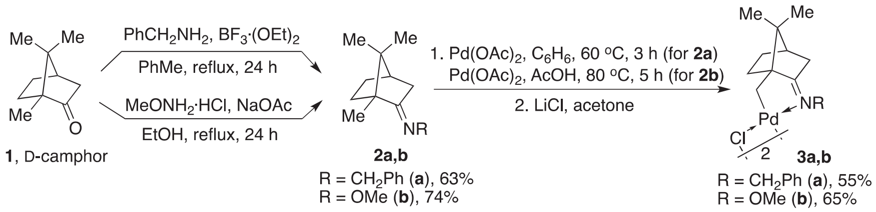
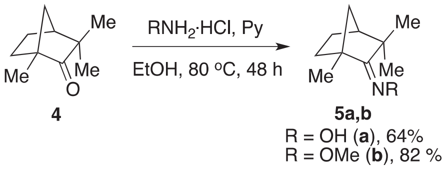


Scheme 1. D-Camphor-derived palladacycles with the (sp^3)C–Pd bond [9,10].



Scheme 2. Preparation of preligands **5a**,**b** from L-fenchone **4**.

well as the fenchone derivative **5b** were confirmed by satisfactory elemental analysis.

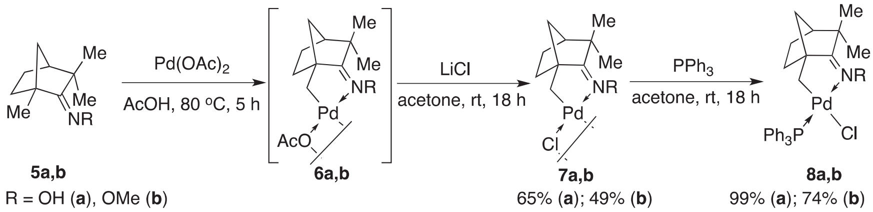
Cyclopalladation of preligands **5a**,**b** and the proposed structures of new complexes **7a**,**b** were supported by NMR spectroscopy. The ^{1}H NMR spectra of oxime **5a** [15] and its *O*-methyl derivative **5b** contained three signals in the region of 1.20–1.35 ppm assigned to the methyl groups at positions 1 and 3. In the ^{1}H NMR spectra of complexes **7a**,**b**, one of the three singlets in that region was replaced by two one-proton signals with the chemical shifts between 2.15 and 2.80 ppm. Compared to preligands **5a**,**b**, the DEPT spectra of dimers **7a**,**b** contained one more CH_2 signal (at 24.6 ppm for **7a** and at 25.8 ppm for **7b**). For comparison, the ^{1}H NMR signals of two diastereotopic hydrogens of the $PdCH_2$ group in the camphor-derived complexes **3a**,**b** appeared at 1.55 and 2.59 ppm (**3a**) and 1.89 and 2.41 ppm (**3b**); the $^{13}C\{^1H\}$ NMR signal of the carbon bonded to the metal in complexes **3a**,**b** was observed at 30.2 and 29.9 ppm, respectively [9,10]. $^{13}C\{^1H\}$ NMR spectra of dimers **7a**,**b** in $CDCl_3$ contained only one set of signals suggesting that these complexes exist in solution as one isomer. For comparison, the $^{13}C\{^1H\}$ NMR spectra of the camphor-derived dimeric complex **3b** in $CDCl_3$ and C_6D_6 contained two sets of signals signifying the existence of this complex in solution as a mixture of syn and anti isomers [9]. The X-ray crystallographic analysis of **3b** revealed the anti geometry of the dimer in solid state [9].

^{1}H, $^{13}C\{^1H\}$ and $^{31}P\{^1H\}$ NMR spectra of mononuclear CPCs **8a**,**b** in $CDCl_3$ contained only one set of signals suggesting that these complexes are single geometric isomers in solutions. The $^{13}C\{^1H\}$ NMR signals assigned to the carbon of the $PdCH_2$ fragment in compounds **8a**,**b** appeared as singlets at 32.8 and 33.0 ppm. The fact that these signals appeared as singlets ($^3J_{C,P} \approx 0$ Hz) may be indicative of the cis position of PPh_3 relative to the methylene group bonded to the palladium [16]. For comparison, the sp^3-hybridized carbons bonded to the metal in the PPh_3 derivatives of **3a**,**b** provided singlets in the $^{13}C\{^1H\}$ NMR spectra at 35.1 and 27.0 ppm, respectively [9,10]. As reported for related PPh_3 derivatives with the (sp^3)C–Pd bond and proven trans-*N*,*P* geometry [17–19], one of the two ^{1}H NMR signals of the $PdCH_2$ group in **8a**,**b** appeared as a doublet ($^2J_{H,H}$ = 10.1 and 10.7 Hz, respectively), while the other hydrogen gave a doublet of doublets due to additional splitting on the phosphorus atom ($^3J_{H,P}$ = 7.2 and 9.0 Hz, respectively). One of the two hydrogens of the $PdCH_2$ fragment in **8a**,**b** provided a signal in a significantly higher field (at 1.09 ppm for **8a** and 0.84 ppm for **8b**) compared to the other hydrogen (2.28 and 2.16 ppm, respectively). The significant signal shift to a higher field for one of the two hydrogens of the $PdCH_2$ group in the ^{1}H NMR spectra of the PPh_3 adducts **8a**,**b** suggests that the hydrogen is under the influence of magnetic anisotropy caused by phenyl groups of the PPh_3 auxiliary ligand. This, in turn, suggests trans-*N*,*P* geometry of complexes **8a**,**b**. For comparison, both ^{1}H NMR signals of the $PdCH_2$ group in the chloro-bridged CPCs **7a**,**b** were observed above 2.15 ppm. To note, the chemical shift of the signals in the $^{31}P\{^1H\}$ NMR spectra of **8a**,**b** (19.70 and 20.32 ppm relative to $P(OEt)_3$, respectively) is within the range reported for related mononuclear CPCs with the (sp^3)C–Pd bond, the PPh_3 auxiliary ligand, and proven trans-*N*,*P* geometry [17–20].

*X-ray structural analysis of complexes **8a**,**b***

Cyclopalladated structure of complexes **8a**,**b** and their trans-*N*,*P* geometry were unambiguously proven by X-ray crystallographic studies. Molecular structures of the complexes and the numbering schemes are presented in Figs. 1 and 2. Selected bond lengths and bond angles are shown in Tables 1 and 2. Crystal, data collection, and refinement parameters for **8a**,**b** are presented in Table 3. The data obtained for complexes **8a**,**b** are compared to those reported for dimer **3b** [9] and the closely related five-membered *CN*-palladacycles **A**–**E** containing the (sp^3)C–Pd bond and PPh_3 as the auxiliary ligand (Chart 1) [17–21].

Bond lengths in **8a**,**b** are similar to those reported for related complexes (Table 1) [9,17–21]. It is noteworthy that the C–Pd bond in complex **8b** is the longest among those found in the related complexes. Interestingly, the Pd–N bond in the same complex **8b** is also the longest among the camphor- and fenchone-derived CPCs **3b** and **8a**,**b**. The Pd–P bond in **8a**,**b** is the shortest among the related *CN*-palladacycles chosen for the comparison (Table 1).



Scheme 3. Preparation of CPCs **7a**,**b** and **8a**,**b** using L-fenchone derivatives **5a**,**b**.