Polyhedron 30 (2011) 2368–2373

Contents lists available at ScienceDirect

Polyhedron

journal homepage: www.elsevier.com/locate/poly

Conformational fluxionality in a palladium(II) complex of flexible click chelator 4-phenyl-1-(2-picolyl)-1,2,3-triazole: A dynamic NMR and DFT study

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ARTICLE INFO

Article history:
Received 7 April 2011
Accepted 13 May 2011
Available online 20 May 2011

Dedicated to Professor Miha Tišler on the occasion of his 85th birthday.

Keywords:
Metallacycle
Palladium
Fluxionality
NMR spectroscopy
Density functional theory calculations

ABSTRACT

An experimental and theoretical DFT study was carried out on the solution behavior in [D$_7$]DMF for bis-chelate complex [Pd(**L**)$_2$](BF$_4$)$_2$·2CH$_3$CN (**L** = 4-phenyl-1-(2-picolyl)-1,2,3-triazole). In structure of [Pd(**L**)$_2$]$^{2+}$, the central square–planar palladium(II) cation is *trans*-chelated by two **L** substrates, each through the pyridine and the triazole N2 nitrogen atoms, forming two six-membered metallacycles. These can adopt boat-like conformations *anti*-*trans*-[Pd(**L**)$_2$]$^{2+}$ and *syn*-*trans*-[Pd(**L**)$_2$]$^{2+}$ in which the picolyl methylene carbons are *anti* or *syn*, respectively, relative to the palladium coordination plane. In solution, the boat-to-boat inversion at both metallacycles takes place. The conformers are in a dynamic equilibrium, which was monitored by variable-temperature (VT) ^{1}H NMR spectroscopy in the temperature range of 223–353 K. The equilibrium lies on the side of the *anti*-*trans*-[Pd(**L**)$_2$]$^{2+}$ conformer and the corresponding reaction enthalpy and entropy is estimated to be 0.6 ± 0.5 kcal mol^{-1} and 0.8 ± 1 cal mol^{-1} K^{-1}, respectively. From the full-line-shape analysis of resonances in the VT ^{1}H NMR spectra, the activation enthalpy and activation entropy was determined to be 13.0 ± 0.4 kcal mol^{-1} and 2.7 ± 1.6 cal mol^{-1} K^{-1}, respectively. The activation entropy close to zero suggests a nondissociative mechanism for the isomerisation. DFT investigation revealed that the isomerisation proceeds through a one step mechanism with a barrier of 11.40 kcal mol^{-1}. The structures of the *syn* and *anti* conformers as well as that of the transition state were characterized. Energy decomposition analysis was carried out in order to explore the origins of the stability difference between the *syn* and *anti* isomers.

1. Introduction

Six-membered chelate rings M(N^N) where N^N are flexible bidentate ligands coordinated to the metals M can adopt different conformations. Such ligands are related to 2,2′-bipyridyl and usually contain 2-pyridyl, 2-imidazolyl or pyrazolyl heterocycles connected by a methylene (CH$_2$) or substituted methylene bridge (Fig. 1). Depending on the metal, the substituents on the heterocyclic rings, as well as the methylene bridge, the conformers of the metallacycle can be in a dynamic exchange. Providing the rate of the exchange is appropriate, the conformers can be detected by NMR spectroscopy. Such examples involving the above mentioned bis-(heterocycle)methane ligands coordinated to square–planar platinum(II) and palladium(II), are well documented [1–4]. The copper(I)-catalyzed 1,3-dipolar cycloaddition [5] of terminal alkynes with organic azides provides a versatile method for the generation of functionalized ligand scaffolds [6]. Appropriately designed 1,4-disubstituted 1,2,3-triazoles can behave as chelators, also referred to as "Click chelators", towards metal ions. Recent reports demonstrate that 4-phenyl-1-(2-picolyl)-1,2,3-triazole (**L**, Fig. 1) can serve as a highly efficient flexible bidentate chelator through the triazole N2 and the pyridyl nitrogen atom. Ligand **L** binds to a variety of metal ions, such as Co^{II}, Ni^{II}, Cu^{II}, Zn^{I}, Ru^{II}, Pd^{II}, Ag^{I}, Pt^{II} and Hg^{II}, forming stable six-membered metallacycles [7–12].

The prominent feature of the solid state structures of these metallacycles is the bowing of the 1-(2-picolyl)-1,2,3-triazole unit, resulting in one of the bridging methylene hydrogens being *anti* and the other *syn* to the metal center [7–12]. In solution, this feature is well preserved in the [RuCl(η^6-*p*-cymene)**L**]OTf complex of a three-legged piano-stool geometry around the ruthenium(II). In this case the bridging CH$_2$ protons of the ligand **L**, bidentately coordinated to ruthenium(II), display two well resolved AB doublets in the ^{1}H NMR spectra. This is expected due to the severe steric crowding between the ligands. In contrast, in sterically less demanding square–planar complexes a rapid inversion of the ligand through a planar M–**L** intermediate is expected, which should lead to the effective equivalence of the methylene hydrogens in solution. Indeed, in the ^{1}H NMR spectra of some 1-(2-picolyl)-1,2,3-triazole complexes of platinum(II), both picolyl protons resonate as an A$_2$ singlet [11,13,14].

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doi:10.1016/j.poly.2011.05.015

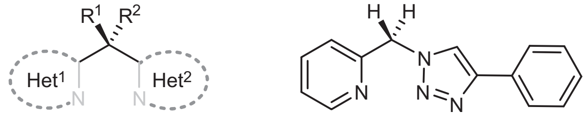


Fig. 1. (Left) General formula of bis-(heterocycle)methane ligands, R^1, R^2 = H, alkyl; Het^1, Het^2 = pyridine, imidazole or pyrazole rings. (Right) 4-Phenyl-1-(2-picolyl)-1,2,3-triazole (**L**).

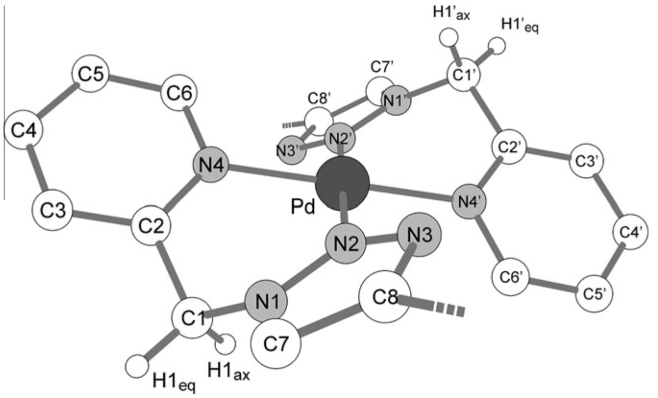
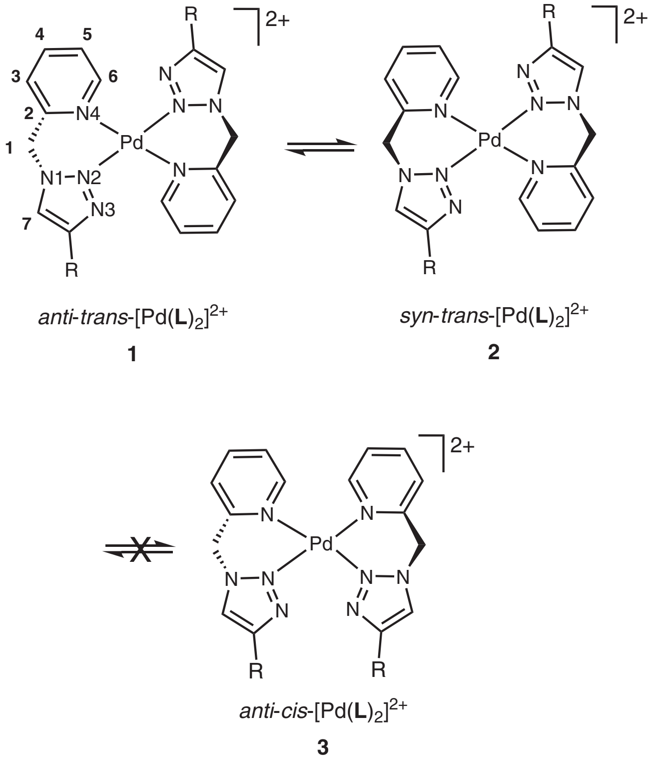


Fig. 2. Selected part of the X-ray crystal structure of $[Pd(\mathbf{L})_2](BF_4)_2{\cdot}2CH_3CN$ [11,16]. The BF_4^- ions and the lattice CH_3CN molecules have been removed for clarity.



anti-trans-$[Pd(\mathbf{L})_2]^{2+}$
1

syn-trans-$[Pd(\mathbf{L})_2]^{2+}$
2

anti-cis-$[Pd(\mathbf{L})_2]^{2+}$
3

Scheme 1. Structures under investigation with the selected atom numbering.

In few instances of "Click chelates", to our knowledge that of square–planar palladium(II) complex $[Pd(\mathbf{L})_2](BF_4)_2$ reported by us (Fig. 2) [11] and platinum(II) complex $[PtCl_2\mathbf{L}]$ by Kilpin and Crowley [15], room temperature ^1H NMR spectra display broadening of the CH_2 singlets. This suggests that a dynamics exchanging the methylene protons occurs at a rate that is relatively slow on the NMR time-scale. Intrigued by these observations, we were prompted to investigate the $[Pd(\mathbf{L})_2](BF_4)_2$ complex experimentally by variable-temperature (VT) ^1H NMR spectroscopy as well as theoretically. The complex undergoes conformational fluxionality at the six-membered Pd–**L** metallacycle. To our knowledge, in complexes with "Click chelators" this phenomenon has not yet been studied despite the fact that these ligands are gaining considerable interest in coordination chemistry [6].

2. Results and discussion

Complex $[Pd(\mathbf{L})_2](BF_4)_2{\cdot}2CH_3CN$ was prepared by the literature procedure from 4-phenyl-1-(2-picolyl)-1,2,3-triazole (**L**) and $[Pd(CH_3CN)_4](BF_4)_2$ in CH_3CN. The X-ray diffraction analysis of this complex revealed a bicyclic structure of the $[Pd(\mathbf{L})_2]^{2+}$ cation, in which the central square–planar palladium(II) is *trans*-chelated by two **L** molecules, each through the pyridine and the triazole N2 nitrogen atoms, forming two six-membered metallacycles. These adopt boat-like conformations, in which the picolyl methylene carbons are *anti* relative to the palladium coordination plane, *anti-trans*-$[Pd(\mathbf{L})_2]^{2+}$ (Fig. 2). The solid-state structure is best presented by the molecular drawing **1**, shown in Scheme 1 (R = Ph) [11].

2.1. NMR experimental study

The variable-temperature (VT) ^1H NMR spectra of $[Pd(\mathbf{L})_2](BF_4)_2{\cdot}2CH_3CN$ were measured in deuterated *N*,*N*-dimethylformamide ($[D_7]$DMF) in the temperature range of 223–353 K, and are shown in Fig. 3. The spectrum at 223 K is consistent with the presence of two isomers of the complex cation $[Pd(\mathbf{L})_2]^{2+}$. Two doublets of the pyridyl H6, two singlets of the triazolyl H7 and two pairs of doublets, belonging to the bridging methylene groups ($H1_{ax}$ and $H1_{eq}$), are clearly visible. The other resonances of both isomers are less separated. Based on the integration, the isomers appear in the molar ratio of 0.73:0.27. The assignment of the resonances is based on our previous work [11]. It is generally accepted that a geminal axial proton in square–planar palladium [17] and platinum [18] complexes with bis(heterocycle)methane ligands appears at lower field compared with the equatorial one, which led us to assign $H1_{ax}$ and $H1_{eq}$ as shown in Fig. 3.

At increase in the temperature, the broadening of the resonances occurs. The H6 and H1 resonances broaden to the baseline with the subsequent appearance of the average resonances above 273 K. After the initial broadening of H7 resonances, going from 223 K to 243 K, on further heating these re-sharpen and appear as a singlet. This behavior suggests that an interconversion between two isomers takes place. Assuming that the structure of one of the isomers corresponds to that found in the solid state of this complex (Fig. 2), [11] the VT ^1H NMR spectra could be rationalized by the Pd–**L** six-membered chelate ring inversion between *anti-trans*-$[Pd(\mathbf{L})_2]^{2+}$ (**1**) and *syn-trans*-$[Pd(\mathbf{L})_2]^{2+}$ (**2**), as shown in Scheme 1 (R = Ph).

For the equilibrium between **1** and **2** in the above model, we determined the thermodynamic parameters ΔH and ΔS, as follows. At 223 K, ΔG of 0.44 kcal mol^{-1} was simply calculated using Eq. (1) from the molar ratio $n_1{:}n_2$ of 0.73:0.27, determined by the integration. In the fast-exchange regime at 353 K, we first calculated (Eq. (2)) the molar ratio between **1** and **2** ($n_1{:}n_2 = 0.615{:}0.385$) using the measured averaged signal of H6 protons ($\delta_{aver.} = 9.22$ ppm) and the calculated chemical shifts δ_1 and δ_2 for both isomers (8.85 ppm and 9.84 ppm, respectively). The latter were obtained from the corresponding values measured at 223 K, corrected by considering the apparent temperature-dependence of the chemical shifts (Fig. 3). From the chemical shifts of pyridyl H4 protons in the fast-exchange regime between 253 K and 353 K, this