SYNTHESIS OF A PALLADIUM(II) COMPLEX OF *N*-(2,7-DIMETHYLOCTADIENYL)BENZIMIDAZOLE

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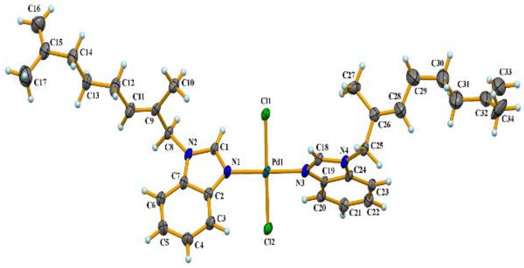
Abstract

Based on *N*-(2,7-dimethyloctadienyl)benzimidazole (**1**), a benzimidazolyl terpene of irregular structure, a palladium(II) complex was obtained in order to study its structure and suitability for biological evaluation. It was found that the volume of ligand **1** is large enough to form a stable *trans*-complex. According to the results of X-ray diffraction analysis, only [1-(2,7-dimethyl-2,7-octadien-1-yl)benzimidazole]palladium(II) dichloride (**2**) of *trans*-configuration is formed.



Key words: irregular terpenoids, benzimidazole, palladium(II) complexes, X-ray diffraction.

Introduction

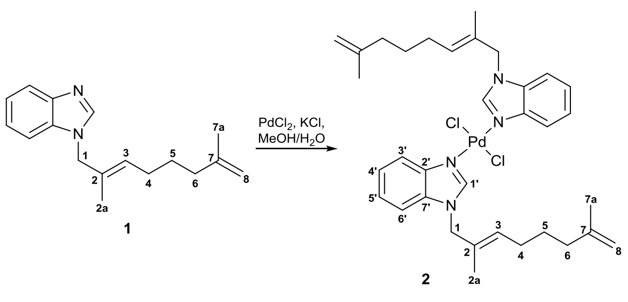
The palladium-catalyzed telomerization of isoprene with amines produces terpenoids with both a 2,6-dimethyloctane backbone, which are called regular terpenoids, and terpenoids with 3,6- and 2,7-dimethyloctane backbones, which are called irregular terpenoids. The overwhelming majority of natural terpenes feature a regular structure, while the number of irregular terpenes isolated from living organisms does not exceed 5–6. Earlier we have suggested the catalysts and conditions that enable the synthesis of *N*,*N*-dialkyl-*N*-(2,7-dimethylocta-2,7-dien-1-yl)amines, providing the selectivity of up to 99%, and obtained *N*-terpenylbenzimidazoles on their basis [1]. Using the terpene derivatives of benzimidazole as the examples, it was shown that the compounds obtained based on the telomers with a 2,7-dimethyloctane backbone exhibit biological activity similar to that of regular terpenes [2–5].

It is well known that Pd(II) complexes bearing substituted aromatic *N*-heterocyclic ligands exhibit potent antitumor activity [6]. Palladium(II) complexes containing terpene units, in addition to antitumor activity, exhibit prominent antibacterial and antifungal properties [7, 8]. In a recent review, Denisov showed [9] that Pd(II) compounds inhibit enzymes involved in the pathogenesis of different diseases, including Alzheimer's and Parkinson's diseases, and also inhibit tumor enzymes, enzymes of HIV-1 and SARS-CoV-2 viruses, sleeping sickness pathogen, putrefactive bacteria, and other microorganisms [9]. It is emphasized that, in contrast to *cis*-platinum(II) compounds, *trans*-palladium(II) complexes are more active, especially in the case benzimidazole derivatives.

Earlier we have suggested the catalyst and conditions for the selective synthesis of *N*-(2,7-dimethyloctadienyl)benzimidazole (**1**) [1]. Considering the large volume of ligand **1**, which can ensure the exclusive formation of a *trans*-complex, it seemed interesting to obtain its Pd(II) complex in order to study its structure and suitability for biological evaluation.

Results and discussion

As a rule, palladium(II) dichloride complexes with aromatic *N*-heterocycles are obtained by the reactions in an aqueous medium. In our case, the reaction of compound **1** with $PdCl_2$–KCl in water gave only a hydrated form of *N*-(2,7-dimethylocta-2,7-dienyl)benzimidazolyl palladium(II) dichloride complex (**2**). However, the reaction in a water–methanol mixture with subsequent treatment of the resulting complex with chloroform enabled the formation of a crystalline form of complex **2** according to Scheme 1.



Scheme 1. Synthesis of *N*-(2,7-dimethylocta-2,7-dienyl)benzimidazolyl palladium(II) dichloride (**2**).

The analysis of the IR spectrum of complex **2** and its comparison with the IR spectrum of the free ligand revealed strong coordination-induced shifts of the imidazole stretches from 1457 and 1441 cm^{-1} to 1485 and 1463 cm^{-1}. The absorption bands corresponding to the vibrations of the internal C=CH bond did not change significantly upon complexation. Thus, the C–H stretches were observed at 2932 (CH_2 unit connected with the double bond) and 3071 cm^{-1} for the ligand

and 2928 (CH_2 unit connected with the double bond) and at 3070 cm^{-1} for the complex, while the C=C stretching vibrations and C–H bending vibrations were detected at 1648 and 640 cm^{-1} for the ligand and at 1647 and 651 cm^{-1} for the complex. The vibrations of the terminal double bond $C{=}CH_2$ differed from those of the internal one only for C–H bending vibrations observed at 886 cm^{-1} for ligand **1** and 882 cm^{-1} for complex **2**. Therefore, the double bonds of the terpene moiety appeared to be almost unaffected upon complex formation. According to the ^{1}H NMR spectral data, significant downfield shifts were observed for the signals of the benzimidazole unit. A singlet of 1'CH proton shifted from 7.88 ppm to 8.34 ppm, while a multiplet signal of 3'CH shifted from 7.81 ppm to 8.57 ppm upon coordination. According to the results of X-ray diffraction analysis, the heterocyclic ligands adopt *trans*-arrangement in the square-planar geometry of the Pd(II) ion (Fig. 1). The benzimidazole planes are turned in different directions relative to the PdN_2Cl_2 plane by 44.4 and 34.9°, which leads to an almost perpendicular arrangement of these fragments relative to each other (the corresponding dihedral angle between these planes is 80.5°). The lengths of C=C double bonds in the aliphatic units are 1.322(5)–1.344(19) Å, which is consistent with the standard value of 1.32 Å. Terminal C30–C34 atoms of one of the 2,7-dimethyloctadienyl substituents are disordered over two positions with unequal occupancies of 0.704(6)/0.296(6).

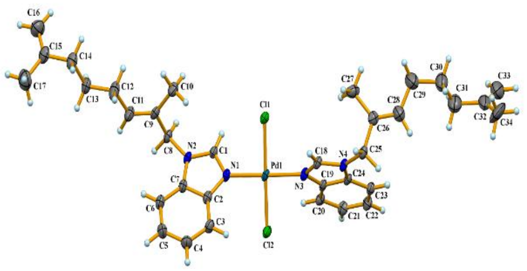


Figure 1. Molecular structure of complex **2**.

Conclusions

Hence, the X-ray diffraction analysis showed that complex **2** features a rigid *trans*-configuration of 1-terpenyl-substituted benzimidazole ligands, which makes it suitable for further bioactivity studies.

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