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| D:\Rinat\Rinat\доки\журнал\статьи\logo.jpg | SYNTHESIS OF A PALLADIUM(II) COMPLEX OF *N*-(2,7-DIMETHYLOCTADIENYL)BENZIMIDAZOLE | | |
| Cite this: *INEOS OPEN*,  **2025**, *8 (1–3)*, 82–83  DOI: 10.32931/io2529a  *Received 3 November 2024,*  *Accepted 6 December 2024*  http://ineosopen.org | | E. A. Petrushkina,\**a* T. V. Strelkova,*a* E. G. Kononova,*a* and F. M. Dolgushin*b* | |
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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.

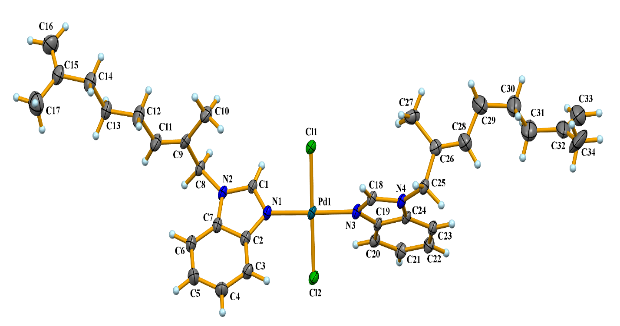
Results and discussion

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 PdCl2–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 (CH2 unit connected with the double bond) and 3071 cm–1 for the ligand and 2928 (CH2 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=CH2 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 1H 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 PdN2Cl2 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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