EurJOC
European Journal of Organic Chemistry

A Journal of ChemPubSoc Europe

Accepted Article

Title: Transformations of meso-iminofunctionalized Pd(II) and Ni(II)-complexes of β-alkylsubstituted porphyrins

Authors: Dina R. Erzina, Ilya A. Zamilatskov, Nadezhda M. Stanetskaya, Vladimir S. Tyurin, Grigory L. Kozhemyakin, Gelii V. Ponomarev, Vladimir V. Chernyshev, and Andrew N. Fitch

To be cited as: *Eur. J. Org. Chem.* 10.1002/ejoc.201801659

Link to VoR: http://dx.doi.org/10.1002/ejoc.201801659

Supported by ACES Asian Chemical Editorial Society

WILEY-VCH

10.1002/ejoc.201801659

WILEY-VCH

Transformations of *meso*-iminofunctionalized Pd(II) and Ni(II)-complexes of β-alkylsubstituted porphyrins

Dina R. Erzina,[a] Ilya A. Zamilatskov, *[a] Nadezhda M. Stanetskaya,[a] Vladimir S.Tyurin,[a] Grigory L. Kozhemyakin,[a] Gelii V. Ponomarev,[b] Vladimir V. Chernyshev,[a,c] and Andrew N. Fitch.[d]

Abstract: The *meso*-imino derivatives of the palladium (II) and nickel (II) complexes of coproporphyrins I and II and β-octaethylporphyrin were obtained by the Vilsmeier formylation followed by interaction with amines. The metal complexes of the azomethines obtained were transformed to the corresponding complexes of cyclopentane and cyclopentane-pyrrolidone fused porphyrin derivatives by thermolysis. The plausible mechanism of such transformations was suggested and substantiated with quantum chemical calculations. *Meso*-cyano-, *meso*-hydroxy- and *meso*-aminocarbonyl derivatives of β-octaethylporphyrin were obtained by treatment of the corresponding *meso*-imino derivatives with bases. Demetalation of the nickel complex of the *meso*-hydroxy-β-octaethylporphyrin led to formation of the free base derivative. The structures of new types of the porphyrin derivatives were determined via X-ray powder diffraction analysis. The obtained types of porphyrins are promising candidates to use as photosensitizers in medicine applications due to their longer wave absorption combined with high stability.

Introduction

Porphyrins and their derivatives are the key compounds providing the energetics of the biosphere. In particular, metal complexes of porphyrins form the basis of the photosynthetic center, transfer oxygen (hemoglobin), catalyze oxidative processes as part of enzymes (cytochromes). The unique properties of the tetrapyrrolic compounds are associated with their multi-electron aromatic system. Photophysical characteristics of porphyrins and their analogues allow to successfully use these dyes as fluorescent/phosphorescent sensors in bioanalysis[1–6], photosensitizers in photovoltaics[7,8], photocatalysis[9,10] and photodynamic therapy of tumors[2,4] and other diseases (acne, psoriasis, atherosclerosis)[11,12].

Insertion of various groups into the tetrapyrrolic macrocycle allows modifications to obtain new derivatives with improved photophysical characteristics[13,14]. One of the most important directions of modification of porphyrins and their derivatives is the formyl group insertion into various positions of the macrocycle. The carbonyl function of the formyl group serves as a modification center for the preparation of compounds containing various groups: vinyl, carboxyl, hydroxyl, etc[15]. There are a large number of examples of the utilization of the formyl group as a precursor for further modifications using following reactions: Wittig[16–20], Grignard[19,21], McMurry[22], Schiff bases formation[23–26], Knoevenagel[27] etc.

Synthesis of Schiff bases of *meso*-formylpophyrins is a particular promising direction of research. *Meso*-iminoporphyrins were applied as oxygen/pH multisensors[28]. Azomethine bridge in bisporphyrins and porphyrin conjugates was shown to provide rapid and efficient excited-state energy transfer while maintaining weak ground state electronic interactions[29–31]. A huge variety of the conjugates of tetrapyrrolic compounds, including those with improved photophysical characteristics can potentially be obtained using imine formation as a bridging tool[32]. Further transformation of the imino-group to other functional groups provides an additional tool for the porphyrin structure and properties tuning.

The investigation of methods of synthesis and applications of *meso*-formyl and *meso*-imino porphyrin derivatives has been conducted in our research group[33,34]. There are two approaches to the synthesis of Schiff bases: the reaction of formylporphyrin with amines and the interaction of the so called "phosphorus complex" with amines. The classical reaction of amines with the aldehyde derivatives of porphyrins was studied on the example of synthesis of oximes, which were obtained with high yields by boiling of the formyl derivatives of porphyrins with hydroxylamine for several hours in aqueous pyridine[19,23,35–37]. Oximes are of interest as precursors for obtaining cyanoporphyrins with the aim of transformation of the latter to carboxy substituted porphyrins and also as starting materials for further synthesis of products of intramolecular cyclization[37].

The reaction of the "phosphorus complex" with amines has become more widespread[23,38]. Azomethine derivatives of formylporphyrins were obtained by direct interaction of the "phosphorus complex" with amines. This method is used in the synthesis of Schiff bases with not only aliphatic amines, but also with hydroxylamine, hydrazine, some amino acids, excluding amino acids which don't react due to sterical hindrance.

The study of mass spectra of Schiff bases is of particular interest. For the first time mass spectrometric study of *meso*-substituted porphyrins was performed by P. Clezy[39], who demonstrated that all *meso*-substituted derivatives of β-octaethylporphyrin (OEP) gave OEP cation in the mass spectra, i.e. *meso*-substituent elimination occurs in the ion source of mass spectrometer with intermolecular hydrogen addition [23,39]. For this reason P. Clezy concluded that it was impossible to study

[a] Laboratory of New Physicochemical Problems
A.N. Frumkin Institute of Physical chemistry and Electrochemistry RAS
31-4, Leninsky prospect, Moscow, 119071 Russia
E-mail: joz@mail.ru
[b] Laboratoty of Synthesis of Physiolological Active Compounds
Institute of Biomedical Chemistry
10/8, Pogodinskaya street, 119121, Moscow, Russia
[c] Department of Chemistry
M.V. Lomonosov Moscow State University
1-3, Leninskie Gory, Moscow, 119991, Russia
[d] European Synchrotron Radiation Facility
BP 220, F-38043 Grenoble Cedex, France

such compounds by mass spectrometry due to their thermal instability. H. Budzikiewicz encountered a similar problem during the study of a large number of mass spectra of porphyrins and chlorins [40]. He suggested that the fragmentation was associated with complex rearrangement processes, but didn't support the assumption by experimental investigations. The first substantial study of the mass spectra of the Schiff bases of *meso*-formylporphyrins was held by G. Ponomarev[41]. He found that all spectra contained ions $[M - NR]^+$ and $[M - RNH_2]^+$, and the intensity of the latter was maximal. Since it was hard to imagine that the molecular ion of the Schiff base disintegrated loosing amine residue with the simultaneous transfer of two hydrogen atoms from the porphyrin cycle to the amine nitrogen atom, intramolecular rearrangements were suggested to occur in two stages. The first stage of fragmentation was the intramolecular rearrangement of the molecular ion into cyclic compounds, which decay led to ions $[M - NR]^+$ and $[M - RNH_2]^+$[23].

For the derivatives of etioporphyrin the presence of ions with mass numbers 490 and 488 corresponding to $[M - NR]^+$ and $[M - RNH_2]^+$ indicated the thermal decomposition of Schiff bases in the ion source of the mass spectrometer with the formation of new compounds containing five-membered exocycle[23]. Thus, due to the detailed analysis of mass spectra of the Schiff bases, the possibility of the transformation of *meso*-imino-substituted porphyrins to cyclopentaneporphyrins has been discovered. It is known that derivatives of porphyrins and chlorins containing additional exocyclic fragments possess unusual photophysical characteristics. Steric distortion of the tetrapyrrolic macrocycle caused by a formation of additional exocycles leads to a change of the energy of the electron transition S0→S1 and, consequently, to a bathochromic shift of the maximum of Q absorption bands. Modification of porphyrins leading to their new derivatives with longer wave absorption would give us new porphyrin dyes possessing useful properties for the application as active substances for the treatment and diagnosis of cancer, sensors and highly sensitive phosphorescent labels for bioanalysis.

Exocycle contained porphyrins were found in fossils and were named as petroporphyrins (geoporphyrins, sedimentary porphyrins). They were derived from naturally occurring chlorophylls[42]. insertion of the exocyclic ring to porphyrins was the subject of numerous works, but multiple synthetic steps are usually required. Among various petroporphyrins synthesis of cyclopentane fused porphyrins proved to be mostly difficult[43]. Synthesis of the exocycles of the porphyrins are often determined by steric factors, as the peripheral substituents in the β and *meso* positions of the tetrapyrrolic compounds located spatially close to each other. This fact allows not only to perform various cyclization reactions, but also to rearrange the substituents at the periphery of the macrocycle. Thus, the development of new methods of porphyrins modification would allow to obtain new useful tetrapyrrolic compounds, thereby significantly expanding their structural diversity, as well as to come to deeper knowledge about the mechanisms of chemical transformations of the entire class of tetrapyrrole compounds.

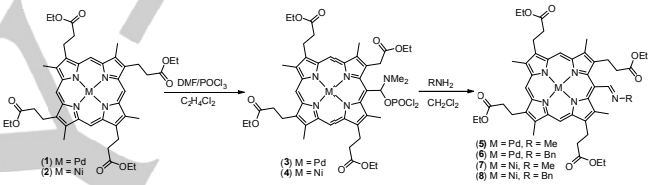
Results and Discussion

1. Preparation of azomethine derivatives of Pd(II) and Ni(II) complexes of coproporphyrins I and II and β-octaethylporphyrin using electrophilic substitution reaction.

Azomethine derivatives of a number of metal porphyrins (Pd(II) and Ni(II) complexes of tetraethyl ester of coproporphyrin I, tetramethyl ester of coproporphyrin II, and β-octaethylporphyrin) were obtained by the reaction of amines (methylamine and benzylamine) with the so called "phosphorus complexes". The latter were obtained by the treatment of the metal porphyrin complexes with the Vilsmeier reagent obtained *in situ* by the interaction of N,N-dimethylformamide and phosphorus(V) oxochloride.

Pd(II) and Ni(II) complexes of tetraethyl ester of coproporphyrin I, tetramethyl ester of coproporphyrin II, and β-octaethylporphyrin were prepared according to the procedure reported [44,45].

Azomethine derivatives of Pd(II) and Ni(II) complexes of tetraethyl ester of coproporphyrin I with methylamine, and benzylamine **(5-8)**, were synthesized as reported [33] (Scheme 1).



Scheme 1. Preparation of azomethine derivatives of Pd(II) and Ni(II) complexes of tetraethyl ester of coproporphyrin I with methylamine and benzylamine.

Reactions proceeded with high yields, formation of by-products was negligible. However, in the case of the Ni(II) complex interaction with the Vilsmeier reagent proceeded for 30 minutes at 45 °C, in contrast to the palladium complex, for which the similar reaction took 18 hours at 79 °C. The structure of the compound **(8)** was studied by X-ray powder diffraction analysis (XRPD) (Figure 1). In the complex **(8)** the Ni atom is located in the plane of the molecular skeleton. The lengths of the Ni–N bonds are: 2.037, 2.112, 1.946, 1.956 Å. The double C=N bond has E-configuration and is orthogonal to the porphyrin core π-system, which excludes π conjugation between them (Figure 1, A).

The crystal packing of the compound **(8)** has a characteristic feature manifested in short unit cell parameter (Figure 1, B). This means that there must be strong interactions between the molecules related by the translation along this parameter that bind them into stacks. The distance between the root-mean-square planes of porphyrin macrocycles in the stacks is 3.63 Å.

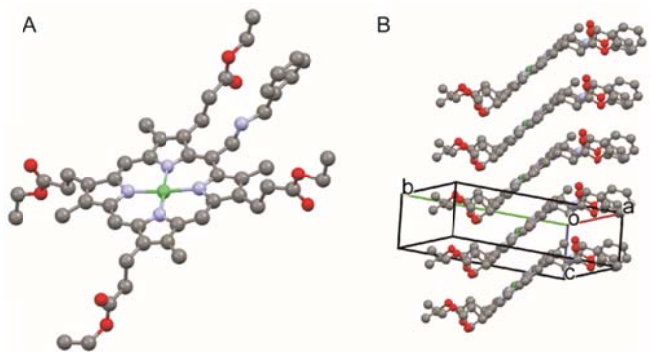
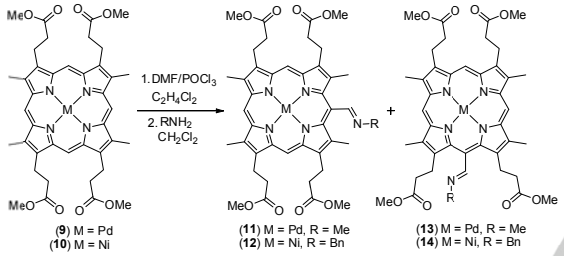


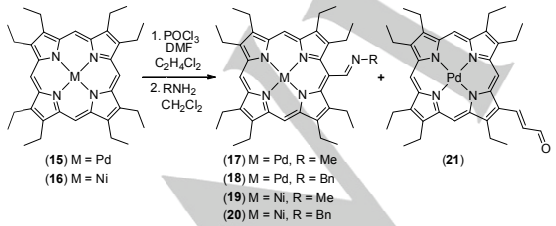
Figure 1. Molecular structure (A) and crystal packing (B) of the Schiff base (**8**) established by XRPD.

Using similar procedures, azomethine derivatives of Pd(II) and Ni(II) complexes of tetramethyl ester of coproporphyrin II with methylamine and benzylamine **(11-14)** were obtained [34,46] (Scheme 2).



Scheme 2. Preparation of azomethine derivatives of Pd(II) and Ni(II) complexes of tetramethyl ether of coproporphyrin II with methylamine and benzylamine.

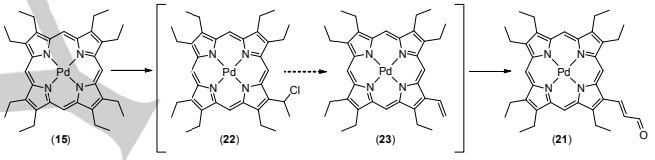
Schiff bases of *meso*-formyl derivatives of the Pd(II) and Ni(II) complexes of β-octaethylporphyrin with methylamine and benzylamine **(17-20)** were obtained by the same procedure (Scheme 3). In the case of the Ni(II) complex, the target products **(19)** and **(20)** were obtained. Pd(II) complex of β-octaethylporphyrin complex gave byproduct **(21)** with 30% yield in addition to the target Schiff base [34].



Scheme 3. Preparation of azomethine derivatives of Pd(II) β-octaethylporphyrin complexes with methylamine and benzylamine.

Target Schiff bases have the similar polarity with the compound **(21)**, so their chromatographic separation was failed. For this reason, isolation of azomethine derivatives **(17)**, **(18)** and compound **(21)** was based on the ability of Schiff bases to interact reversibly with alkyl halides with the formation of corresponding iminium salts. The latter were obtained by addition of iodomethane to the mixtures of products **(17)** + **(21)** and **(18)** + **(21)**. The resulting salts were more polar relative to the product **(21)**, which didn't form a salt, so the chromatographic separation was easy. The reverse formation of Schiff bases from their salts proceeded rapidly by the addition of the corresponding amine in dichloromethane.

Formation of the product **(21)** resulted, apparently, via a number of transformations occurred under the conditions of the Vilsmeier-Haack reaction. The possible pathway of the formation of this compound is shown at Scheme 4. The Vilsmeier reagent is not only a formylating but also a chlorinating agent, therefore, the chlorination of the ethyl group with the formation of a monochlorinated derivative presumably took place at the first stage. Following dehydrohalogenation led to formation of a vinyl group, which was subjected to formylation in the next step (Scheme 4).



Scheme 4. A possible pathway of formation of the compound **(21)**.

2. Synthesis of cyclopentane derivatives of β-alkylporphyrins by thermolysis.

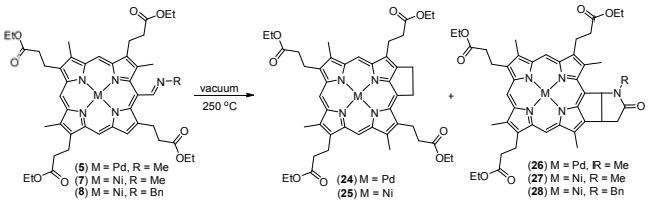
The reaction of intramolecular cyclization of azomethine derivatives of porphyrins was first discovered by Ponomarev during the study of mass spectra of azomethine derivatives of porphyrins and chlorins. Later Ponomarev reproduced the reaction in a laboratory synthesis at low pressure and high temperature.[35,47] In the present work we investigated this process and developed an optimized procedure for the preparation of the cyclopentane fused porphyrin derivatives.

The thermolysis reaction was carried out for Pd(II) and Ni(II) complexes of azomethine derivatives of tetraethyl ester of coproporphyrin I **(5**, **7**, **8)**. In heating at low pressure, a boiling melt was formed, which solidified upon cooling. Formation of target compounds was observed after 10 minutes. After 5 minutes the yield of the target products was maximal and the tar was formed in insignificant amount.

Pd(II) complex gave yields: 13% of the cyclopentaneporphyrin **(24)** and 19% of the lactam **(26)**. In this case, the main part of the reaction mixture was the initial azomethine derivative, which could be isolated and re-used in the thermolysis reaction. Cyclization products from the Pd(II) complex of azomethine derivative of the tetraethyl ester of coproporphyrin I with benzylamine weren't formed during thermolysis under various

conditions. Absorption spectra of the reaction mixture contained bands of chlorins, but isolation of the chlorins was failed.

The cyclopentaneporphyrin **(25)** with 17% yield and the cyclic lactams **(27)**, **(28)** with 32% and 30% yields respectively were obtained from the azomethine derivatives of Ni(II) complexes of tetraethyl esters of coproporphyrin I **(7)** and **(8)** (Scheme 5). In addition to thermolysis products, the initial azomethine derivatives and *meso*-methyl derivatives were found in the reaction mixture in small amounts. Crystal structures of compounds **(25)** and **(27)** were determined by XRPD (Figure 2). It was shown that the root-mean-square planes of the lactam cycle and the porphyrin ring in the compound **(27)** were inclined to each other at an angle of 73(1)° (Figure 2, B), while the cyclopentane fragment of the compound **(25)** lied in the plane of the porphyrin ring (Figure 2, A).



Scheme 5. Synthesis of cyclopentaneporphyrins **(24-25)**, and lactams **(26-28)** by thermolysis.

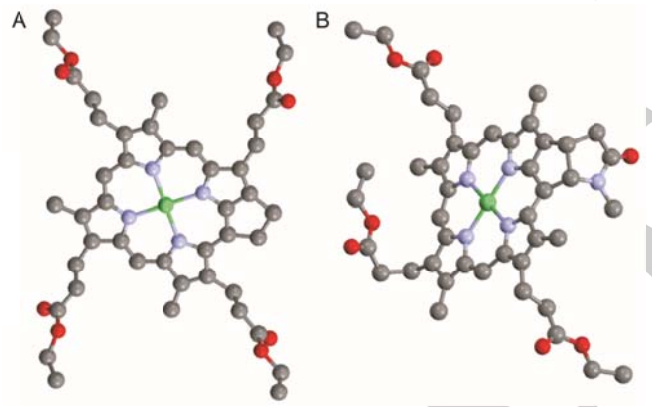
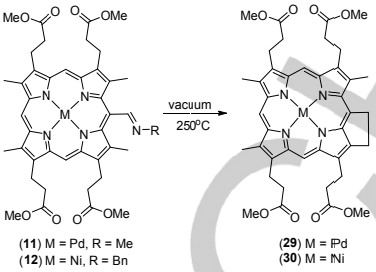


Figure 2. Molecular structures of cyclopentaneporphyrin **(25)** (A) and lactam **(27)** (B) determined by XRPD.

In the case of the thermolysis of Pd(II) and Ni(II) complexes of tetramethyl ester of coproporphyrin II **(11, 12)**, as expected, only cyclopentaneporphyrins **(29, 30)** (Scheme 6) were formed with 14% and 44% yields respectively. The conversion of Pd complex **(11)** was negligible and most of the reaction mixture was the starting material. Pd(II) complexes of the methylamine and benzylamine azomethine derivatives of β-octaethylporphyrin **(17, 18)** couldn't be thermolysed because they sublimated bypassing the molten state.

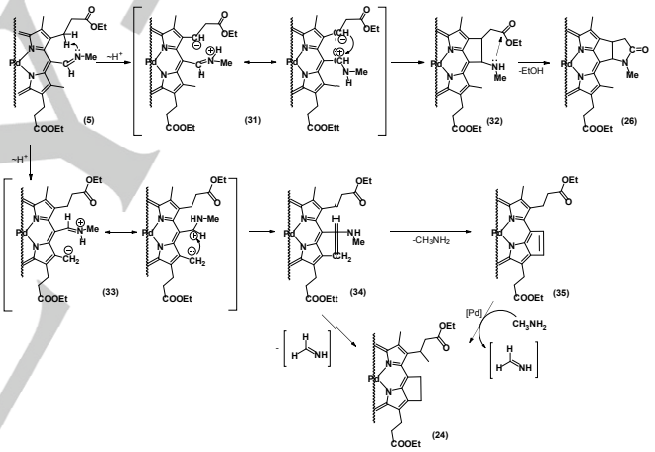
Investigated thermolysis reactions provide the short and simple method of the synthesis of 5-member ring fused porphyrins possessing useful photophysical properties such as bathochromically shifted UV-Vis absorption spectra.



Scheme 6. Synthesis of the cyclopentaneporphyrins **(29)**, **(30)**.

3. Plausible mechanisms of the thermolysis reaction

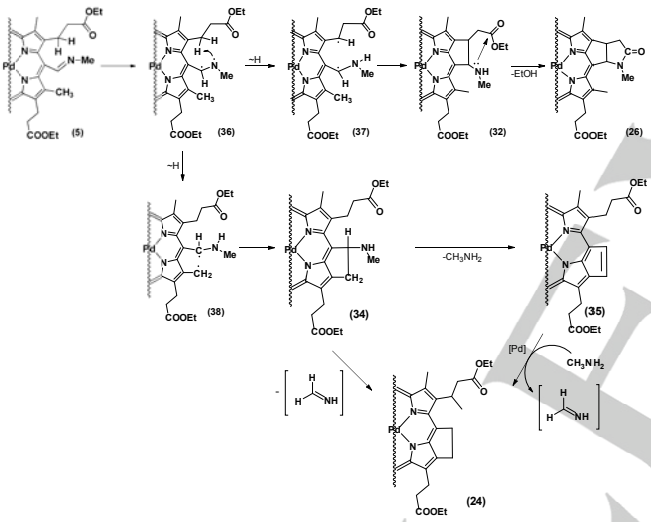
We suggested two possible pathways of the formation of the exocyclic porphyrins: ionic and radical. The ionic pathway is shown on the example of compound **(5)** at Scheme 7.



Scheme 7. Plausible ionic mechanism of the thermolysis reaction.

The first stage involved the proton transfer from the α-carbon of the β-substituent to the nitrogen atom of the azomethine group to form intermediates **(31)** and **(33)**. The negatively charged α-carbon atom of the substituent at the β-position of the porphyrin attacked the electrophilic carbon atom of the iminium group to form the cyclopentane ring. Further development depends on what type of the substituent was deprotonated. In the case of deprotonation of the terminal methylene carbon of the ethyl propanoate group leading to intermediate **(31)**, after the formation of the cyclopentane **(33)** newly formed amino group interacted with the neighboring ester group with the formation of the lactam cycle **(26)**. If β-methyl group had been deprotonated forming the intermediate **(33)**, then the cyclopentane intermediate **(34)** was formed, which was unstable under the reaction conditions and transformed to the product **(24)**. This process can proceed either as a reductive elimination of the methyleneimine from the compound **(34)** or as a two-stage

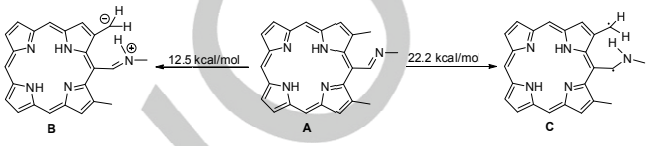
process, including the elimination of the methylamine to form **(35)** with subsequent catalytic hydrogenation of the double bond of the exocycle (Scheme 7). The latter process is quite possible under the reaction conditions. Catalytic hydrogenation of alkenes using amines as hydrogen donors was reported in literature [48]. Nickel and palladium metals were able to be partially released due to some extent of destruction of metal complexes of porphyrins at high temperature of reaction conditions. These metals are well-known hydrogenation catalysts. Higher yields of exocyclic porphyrin derivatives with nickel complexes can partially be explained by their lower stability under thermolysis compared to palladium complexes, one of the consequences of which is higher release of nickel metal catalyzing the hydrogenation process. This hypothesis is also supported by the formation of a number of other hydrogenated byproducts including chlorins, which were observed in the visible absorption spectra of the reaction mixture. Participation of metals in the transformations was clearly confirmed by the fact that thermolysis of free base porphyrins failed.



Scheme 8. Plausible radical mechanism of the thermolysis reaction.

In the case of the radical mechanism, a homolytic break of the double azomethine C=N bond of the compound **(5)** occurs under the action of temperature leading to formation of the biradical **(36)** (Scheme 8). Then, the nitrogen atom takes the hydrogen atom from the α-carbon of the β-substituent to form more stable benzylic biradicals **(37)** and **(38)**. Subsequent intramolecular recombination of radicals leads to the formation of cyclopentane ring. Further transformations proceed as in the previously described ionic scheme (Scheme 7). Both mechanisms can explain the formation of chlorins in the thermolysis reaction of the Pd(II) complex of the benzylamine azomethine derivative of the tetraethyl ether of coproporphyrin I. The benzylamine molecule is significantly heavier than methylamine, and therefore is less volatile and is removed from the reaction mixture much slower and to a lesser extent. Amines are hydrogen donors and the presence of benzylamine in higher amount leads to the catalytic reduction of thermolysis products to various chlorins to a larger extent compared to methylamine derivatives.

In order to clarify the mechanism of the thermolysis transformation quantum chemical calculations of the intermediates were carried out by DFT methods. To simplify the calculations, first we constructed a rough model compound 5-((N-methylimino)methyl)-3,7-dimethylporphyrin **A** (Scheme 9).



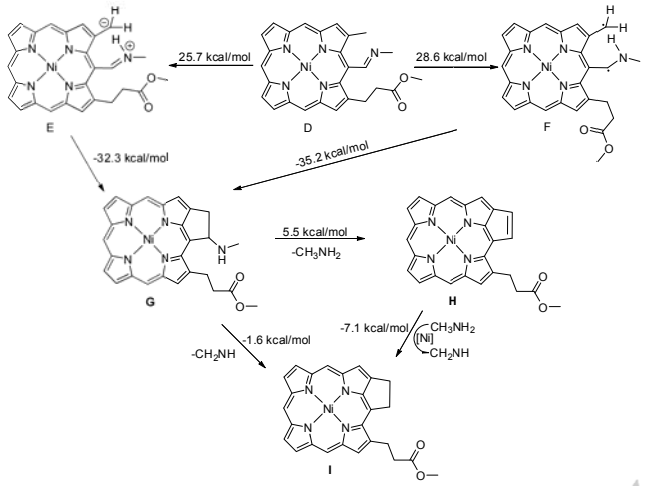
Scheme 9. Heterolytic vs. homolytic pathways.

The geometries were optimized and the energies of the model compound and primary intermediates of homo- and heterolytic pathways of the reaction were calculated by the B3LYP/3-21G method both in vacuum and in nitrobenzene solution at +250 °C. The nitrobenzene was used to model the molten reaction mixture as it fairly close in polarity to the investigated compound. The key stage of the process was the hydrogen transfer from the α-carbon of the β-substituent to the nitrogen atom of the imino group. The hydrogen can pass with or without electrons leading to the biradical or betaine intermediate correspondingly. The choice of the type was based on the relative energies of the corresponding intermediates. The Gibbs free energy change of the reaction **A** → **B** was 12.5 kcal/mol and that of **A** → **C** was 22.2 kcal/mol (Scheme 9). The betaine intermediate B was by almost 10 kcal/mol lower in energy than the biradical **C** at both +250 °C and standard conditions. The energy difference was slightly less in vacuum compared to nitrobenzene solution.

Next we designed a closer model compound Ni(II) complex of 5-((N-methylimino)methyl)-3-(2-(methyloxycarbonyl)ethyl)-7-methylporphyrin **D**. The geometries and the energies of the starting compound **D**, product **I** and all intermediates of the reaction were calculated by the B3LYP/6-31G(d,p) method in vacuum. Changes of Gibbs free energies for all suggested stages of the thermolysis are given at Scheme 10. Betaine intermediate is about 3 kcal/mol more stable compared to the biradical. The energy difference between homolytic and heterolytic pathways is less for the Ni complex model than the free base model. The cyclization process from the starting compound **D** to the intermediate **G** is energetically favored (change of Gibbs free energy of the cyclization reaction amounts to -6.6 kcal/mol). Subsequent methyleneimine loss is also favorable (ΔG = -1.6 kcal/mol). However, the direct elimination is unlikely, instead at high temperature the endothermic methylamine elimination (5.5 kcal/mol) can occur and subsequent exothermic hydrogenation (-7.1 kcal/mol) provides overall energetic profit.

Thus the quantum chemical calculations supported the suggested mechanism of the transformation observed at

thermolysis. The calculations revealed that at first stage the proton transfer was slightly more favorable than the homolytic transfer of hydrogen atom. Expected larger difference in the energies of the corresponding transition states supported predominance of the heterolytic pathway, although some part of the reaction could proceed by the homolytic pathway as the energy difference wasn't significant taking into account relatively high temperature +250 °C.

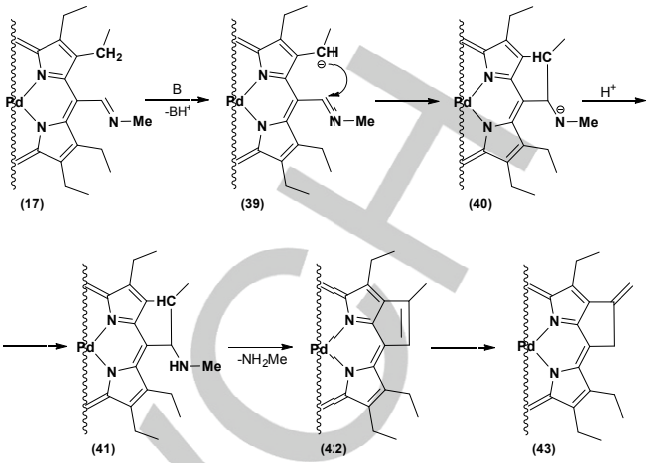


Scheme 10. Scheme of the transformations suggested at thermolysis.

4. Interaction of azomethine derivatives of porphyrins with bases.

To confirm the ionic type of the mechanism of the thermolysis reaction we attempted to synthesize cyclization products through the interaction of azomethine derivatives with various bases. Azomethine derivatives of Pd(II) and Ni(II) complexes of β-octaethylporphyrin with methylamine and benzylamine were used as model compounds.

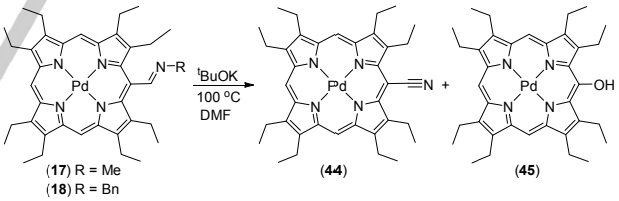
It was assumed that the strong base would abstract the proton from the α-carbon of the β-alkyl group **(39)**. Then the nucleophilic carbanion would attack electrophilic carbon atom of the azomethine fragment to form a cyclopentane ring. Subsequent protonation of the nitrogen anion would lead to the compound **(41)**. Further elimination of methylamine would lead to the cyclopentene derivative which would transform to the less strained exomethylene cyclopentane (Scheme 11).



Scheme 11. Suggested mechanism of interaction of bases (B) with azomethine derivatives of palladium complex of β-octaethylporphyrin.

Experiments were carried out with different bases: *t*-BuOK, *t*-BuOLi, Bu_4NOH, 1,8-diazabicyclo[5.4.0]undec-7-ene (DBU). DMF and 1,4-dioxane were used as solvents. The reaction was carried out by heating to 100 °C for a one minute, then neutralization of the base and isolation of the products were immediately carried out. The reaction didn't proceed with *t*-BuOLi and DBU due to their low basicity and *t*-BuOK and Bu_4NOH worked well.

Two products were formed after the interaction of Pd (II) complexes of azomethine derivatives of OEP, regardless of the substituents at the nitrogen atom (methylamine or benzylamine) (Scheme 12).



Scheme 12. Interaction of Pd(II) complexes of azomethine derivatives **(17)** and **(18)** with a strong base.

The structure of the compound **(45)** was determined by the XRPD and also confirmed using IR, UV-Vis spectroscopy, and MALDI-TOF mass spectrometry. Almost all non-hydrogen atoms of the compound **(45)**, excluding methyl atoms, lie in the same plane (Figure 3). Due to the extremely low solubility of the compound (**45**) in all available deuterated solvents, its NMR spectrum could not be obtained. In this regard, it was decided to repeat the experiments with Ni complexes, as they have greater solubility in most cases.

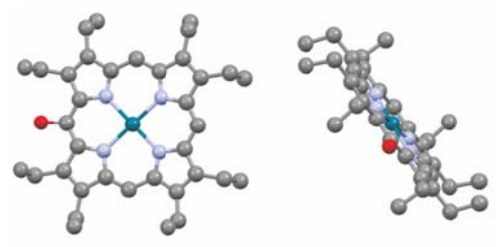
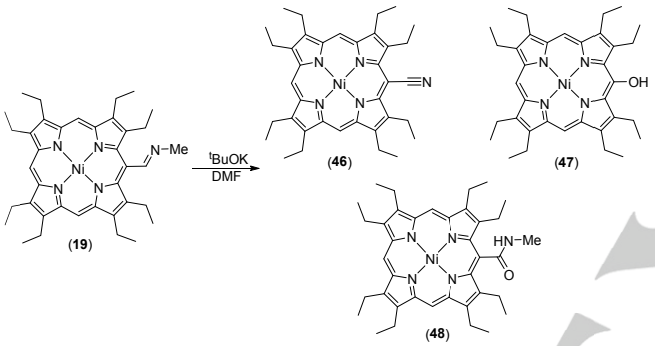


Figure 3. The molecular structure of the compound **(45)** determined by XRPD.

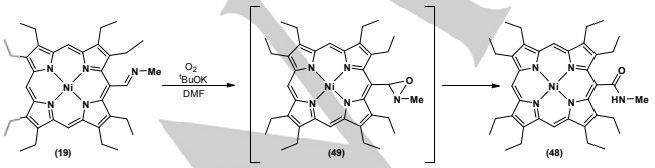
The interaction of Ni(II) complex **(19)** with *t*-BuOK, as well as in the case of Pd(II) complex, resulted in two expected products **(46)** and **(47)**. A peculiarity of the interaction of the Ni complex **(19)** with the base was the formation of a third reaction product - polar porphyrin with an amide substituent **(48)** (Scheme 13).



Scheme 13. Interaction of the Ni (II) complex of azomethine derivative of β-octaethylporphyrin with methylamine **(44)** with a strong base.

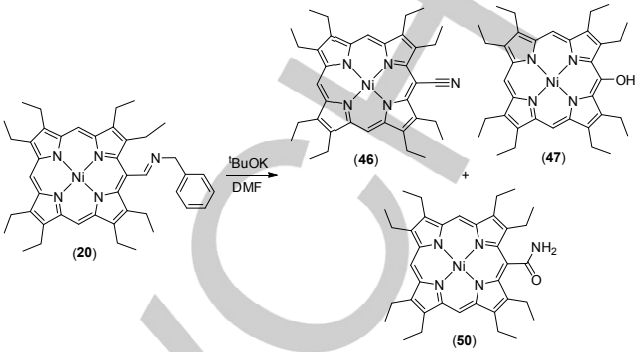
Compound **(48)** was characterized with UV-Vis, NMR spectroscopy and MALDI-TOF mass spectrometry. The solubility of the compound **(47)** was slightly increased compared to **(45)**, but still insufficient to obtain solution NMR spectrum.

After determination of the structure of amide **(48)**, it became clear that the reaction involved not only the base, but also probably air oxygen, causing formation of the oxidation products. It was suggested that the first step was formation of oxaziridine cycle, which rearranged to the amide **(48)** by a radical reaction with participation of oxygen (Scheme 14).



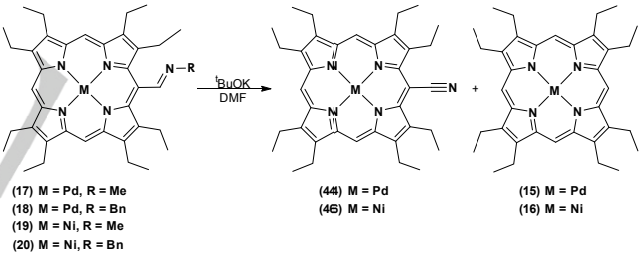
Scheme 14. A possible pathway of formation of the compound **(48)**.

In contrast to the methylamine derivative **(19)**, treatment of the benzylamine azomethine derivative of the Ni(II) complex of OEP **(20)** led to the compound **(50)** with an unsubstituted amide group at *meso*-position (Scheme 15).

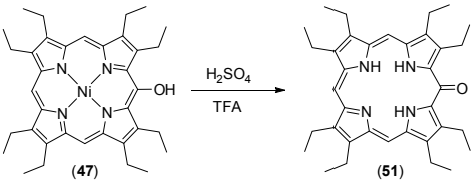


Scheme 15. Treatment of the benzylamine azomethine derivative of the Ni(II) complex β-octaethylporphyrin **(48)** with a strong base.

In order to prove the participation of air oxygen in the reactions of azomethine porphyrin derivatives with strong bases, all reactions were reproduced in dry oxygen free solvents in the argon atmosphere. As a result, nitriles **(44)**, **(46)** were obtained as main products and the initial *meso*-unsubstituted Pd(II) and Ni(II) complexes in small amounts (Scheme 16). Thus, the compounds **(45)**, **(49)**, **(48)** and **(50)** were the products of the interaction with air oxygen.



Scheme 16. Interaction of β-octaethylporphyrin azomethine derivatives with a strong base in dry DMF in an inert atmosphere.



Scheme 17. Demetalation of the Ni complex of *meso*-hydroxyporphyrin (**47**).

Complexes of *meso*-hydroxyporphyrins **(45)** and **(47)** were demetalated with sulfuric acid (Scheme 17). The Pd complex **(45)** was partially destroyed and nothing was isolated. The less stable Ni complex (**47)** was easily demetalated with a solution of

sulfuric acid in trifluoroacetic acid, resulting in formation of *meso*-oxophlorin **(51)** with a quantitative yield.

UV-Vis absorption spectra of all the *meso*-hydroxyporphyrin derivatives are markedly different (Figure 4). Spectra of **(45)** and **(47)** are typical for the metal complexes of *meso*-hydroxyporphyrins: two Q bands are observed at the region 500-600 nm. After removing the metal, a dramatic bathochromic shift of absorption bands occurred to the long-wave region by 94 nm which was a consequence of the tautomerization from the porphyrin to the phlorin with highly disturbed electron structure.

Thus a novel robust method of the *meso*-functionalization of porphyrins was developed leading to the corresponding cyano, amido and hydroxy substituted porphyrins. The *meso*-functionalization expectedly resulted in the red shift of the UV-Vis absorption spectra[49] which could be useful for the photosensitizing applications.

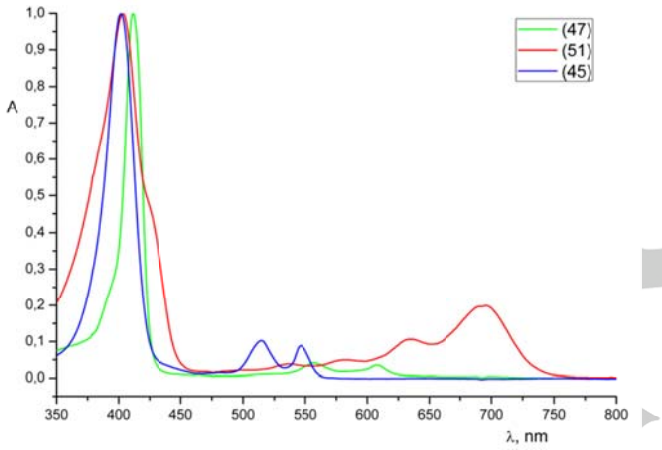


Figure 4. UV-Vis absorption spectra of *meso*-hydroxyporphyrins **(45)**, **(47)**, **(51)** in dichloromethane.

Conclusions

The new types of the porphyrin transformation and functionalization were developed which open up simple possibilities for obtaining easily accessible diverse porphyrin derivatives. Cyclopentane fused porphyrins were obtained through the heating iminoporphyrins. Transformations of the *meso*-iminoporphyrins to the corresponding cyano, amido and hydroxy derivatives have been discovered using interaction with bases. The useful outcome of such functionalization is the longer wave absorption. Such porphyrins with the absorption maximum being around 700 nm are promising candidates to use as photosensitizers in medicine applications (photodynamic therapy etc). Now applied longer wave absorption dyes are usually chlorins. They are not as stable as porphyrins and easily susceptible to oxidation. Therefore, the easy access to the stable porphyrins with photosensitizer ability comparable to chlorins is hard to overestimate.

Experimental Details

General Methods. ^{1}H and ^{13}C NMR spectra were recorded with a Bruker Avance III 600 MHz spectrometer at room temperature. Chemical shifts are reported relative to signals of residual protons of solvents ([D_6]DMSO – 2.50 ppm, $CDCl_3$ – 7.26 ppm). Mass spectra were recorded with UltrafleXtreme mass spectrometer (Bruker Daltonics) in a positive-ion mode using reflection mode with 20 MV voltage without matrix. Electronic absorption spectra were recorded with U-2900 (Hitachi) and UV-4 (Unicam) spectrophotometers in quartz rectangular cells of 10 mm path length.

X-ray diffraction study. Single crystals of the compounds **(8)**, **(25)**, **(27)** и **(45)** were failed to be grown and there were obtained their polycrystalline samples suitable for the determination of crystal structures by X-ray powder diffraction analysis (XRPD)[50–54]. All powder diffraction measurements were carried out at the ID22 high-resolution station at the European synchrotron radiation facility ESRF (Grenoble, France) at 250 K. The station is equipped with a cooled dual silicon Si 111 monochromator and Si 111 analyzer[55]. The powder was poured into a thin-walled borosilicate capillary with a diameter of 1 mm, which during the measurements was rotated at a speed of 1200 rpm to achieve better counting statistics. Calibration of the goniometer and refinement of the X-ray wavelength were performed on a standard silicon sample NIST Si 640c. Indexing was performed using the programs TREOR90[56], ITO[57] and AUTOX[58]. Preliminary refinement by Pawley method[59] confirmed the correctness of the unit cell dimensions and space groups. The crystal structures were solved by simulated annealing technique[60] following the methodology described by us earlier[61,62]. The solutions found were then refined by the Rietveld method with the MRIA program[63], the peak profiles were described by the modified Voight function[64]. The contribution of the texture effect was taken into account by the March-Dollase approach[65]. The anisotropy of the broadening of the diffraction peaks were estimated by the N. Popa model[66]. In the process of refinement, restrictions were imposed on the permissible deviations of interatomic distances in the molecule and on the planarity of individual fragments of the molecule as described in[61,62]. After several cycles of refinement, maps of the differential electron density were analyzed, and if free-standing maxima were found, then an oxygen atom was placed in this position, for which, along with the coordinates, the occupancy factor was refined to find possible residues of solvent molecules. After finding all non-hydrogen atoms and specifying their positions, the positions of hydrogen atoms were calculated, in which they were placed and were not further refined. The crystal data, data collection and refinement parameters for **(8)**, **(25)**, **(27)** и **(45)** are given in Table 1. The geometric parameters of all molecules have normal values comparable to those found in the Cambridge Structural Database [67] for related compounds. In non-symmetrical complexes **(25)**, **(27)** и **(45)** the M(II) cation (M = Ni, Pd) is situated on the center of pseudo symmetry, as was recently observed in the single-crystal structure of Pd(II) complex of 2,3,7,8,12,13,17,18-octaethyl-5-((methylimino)methyl) porphyrin[46]. The locations of some fragments in the molecules in the crystal structures **(25)** (cyclopentane) and **(27)** (lactam and etoxycarbonylethyl) are disordered with equal occupancies (0.5/0.5) over two positions related by crystallographic center of symmetry, thus, showing once again that disorder is an essential feature that greatly affects the formation of the crystal[68,69]. Slightly more complex nature of disorder in **(45)**, where hydroxy oxygen is also disordered over two independent positions with occupancies refined to 0.359(17) and 0.141(17), respectively, leads to the crystal packing close to that in triclinic B polymorph of 2,3,7,8,12,13,17,18-octaethylporphinato-nickel(ii)[70].

Table 1. Crystallographic data for compounds **(8)**, **(25)**, **(27)** and **(45)**.

	(8)	**(25)**	**(27)**	**(45)**
Formula	$C_{52}H_{60}N_5NiO_8 \cdot CH_4O$	$C_{45}H_{52}N_4NiO_8$	$C_{44}H_{49}N_5NiO_7$	$C_{36}H_{44}N_4OPd$
M_r	973.80	835.62	818.59	655.18
Syngony	Triclinic	Monoclinic	Monoclinic	Triclinic
Symmetry group	*P1*	$P2_1/c$	$P2_1/c$	*P-1*
Unit cell dimensions:				
a, Å	14.9403(12)	4.8770(7)	15.2160(11)	13.3198(12)
b, Å	17.8956(15)	30.2813(19)	4.8716(8)	13.4374(12)
c, Å	4.8834(7)	14.2376(11)	26.8336(18)	4.7959(8)
α, °	95.387(11)	90	90	91.921(14)
β, °	94.915(13)	98.944(8)	101.918(15)	93.592(12)
γ, °	76.879(9)	90	90	113.199(17)
V, Å^3	1263.2(4)	2077.1(4)	1946.2(4)	785.84(16)
Z	1	2	2	1
Diffractometer	ID22, ESRF	ID22, ESRF	ID22, ESRF	ID22, ESRF
Wavelength, Å	0.399996(4)	0.399996(4)	0.399996(4)	0.399962(4)

ρ_{calc}, g/cm^3	1.280	1.336	1.397	1.384
μ, mm^{-1}	0.087	0.103	0.109	0.123
$2\theta_{min} - 2\theta_{max}$, $\Delta 2\theta$, ^{o}	0.501 – 20.001, 0.003	0.501 – 20.001, 0.003	0.999 – 20.001, 0.003	1.500 – 20.000, 0.002
Number of parameters / restraints	258/193	153/105	167/132	151/97
$R_p/R_{wp}/R_{exp}$	0.0363/0.0522/0.0125	0.0317/0.0415/0.0182	0.0387/0.0505/0.0179	0.0354/0.0483/0.0190
GoF	4.177	2.285	2.817	2.536

Quantum-chemical calculations

Quantum-chemical calculations of geometry and electronic structure were made within the framework of the density functional theory (DFT) method. The calculations used the hybrid functional B3LYP with the Becke's exchange functional[71] and the correlation functional of Lee, Yang and Parr[72]. For all atoms, a full-electron basis sets 3-21G and 6-31G** with the addition of polarization d, f-orbitals, and p-orbitals for hydrogen atoms were used. The geometry of all studied molecules was fully optimized, the absence of imaginary frequencies confirmed their stationary character. The software package Gaussian 03 was used for calculations.[73] After the procedure of optimization of geometrical parameters wave function stability tests were carried out then calculation of thermochemical parameters was performed. Calculations in nitrobenzene solution were carried out by the same methods using the polarized continuum (PCM) model. The energies of the calculated compounds were corrected for zero vibrational energy (ZPVE) and with thermal corrections to enthalpy and free energy were calculated at the reaction conditions (523.15 K, 1 atm.)

Synthetic procedures

Compounds **(1-2)**, **(5-8)**, **(9-10)**, **(11-14)** were synthesized according to reported procedures [33,34,46]. Compounds (**15**), (**16**) were obtained from commercial sources. Products **(25)**, **(27)**, **(28), (30), (51)** had NMR spectra in agreement with published data [23,35,47,74].

Synthesis of azomethines: The Vilsmeier reagent, in situ formed from 1 ml (0.011 mol) of $POCl_3$ and 1 ml (0.013 mol) of DMF, was added to a solution of 50 mg (0.078 mmol) of Pd(II) complex of β-octaethylporphyrin (**15**) in 40 ml of dry 1,2-dichloroethane at 76 °C. The resulting mixture was stirred for 6 hours at the same temperature and the reaction was monitored by TLC with the eluent CH_2Cl_2/EtOH 100:4. After the reaction completion, the solvent was evaporated in vacuum and 25 ml of distilled water was added to the residue. The organic phase was extracted with dichloromethane and dried over anhydrous sodium sulphate. After filtration and evaporation of the solvent, the residue was dissolved in dichloromethane (30 ml) and methylamine (5 ml of 33% solution in ethanol) was added to the solution at room temperature. The reaction was monitored by TLC with the eluent CH_2Cl_2/EtOH 100:1. After the reaction completion, a mixture of azomethine derivative (**17**) and compound (**21**) was isolated by flash chromatography in dichloromethane. To separate the products, 5 ml of methyl iodide was added to the mixture obtained and the solution was heated at 40 °C for 5 hours until complete transformation of the Schiff base **(17)** to the salt (TLC monitoring). After that, the mixture was evaporated in vacuum, and the compound **(21)** was isolated by flash chromatography in dichloromethane, then the Schiff base salt was washed off the silica with ethanol. Ethanol was evaporated in vacuum, the residue was dissolved in dichloromethane (10 ml) and methylamine (1 ml of 33% solution in ethanol) was added. After 1 hour the organic solution was washed with an aqueous solution of citric acid to get rid of an excess amine, dried with Na_2SO_4 and evaporated in vacuum to give 29.7 mg (56%) of the product **(17)**.

Pd(II) complex of 5-(N-methyliminomethyl)-2,3,7,8,12,13,17,18-octaethylporphyrin (17): NMR ^{1}H (600 MHz, $CDCl_3$), δ, ppm: 1.90-1.95 (24H, m, CH_2-CH_3), 4.04-4.08 (19H, m, CH_2-CH_3 and CH=N-CH_3), 10.06 (1H, s, *meso*-H), 10.09 (2H, s, *meso*-H), 10,94 (1H, d, CH=NCH_3). MS (MALDI-TOF), m/z: 680.3. Calcd. for $C_{38}H_{48}N_5Pd$ ($[M+H]^+$) 680,295. UV-Vis (CH_2Cl_2), λ_{max}, nm (log ε): 397 (5.03), 515 (3.94), 550 (4.30).

Pd(II) complex of 2-(3-oxo-1-propenyl)-3,7,8,12,13,17,18-heptaethylporphyrin (21): NMR ^{1}H (600 MHz, $CDCl_3$), δ, ppm: 1.88-1.95 (21H, m, CH_2-CH_3), 4.05-3.92 (16H, m, CH_2-CH_3), 7.37-7.33 (1H, dd, CHCHCHO), 8.84 (1H, d, β-CH), 9.92 (1H, s, *meso*-H), 9.98 (1H, s, *meso*-H), 9.99 (1H, s, *meso*-H), 10.02 (1H, s, *meso*-H) 10.17 (1H, d, CHO). MS (MALDI-TOF), m/z: 665.2479. Calcd. for $C_{37}H_{43}N_4OPd$ ($[M+H]^+$) 665.2472; UV-Vis (CH_2Cl_2), λ_{max}, nm ($A_{rel.}$): 415 (1.00), 517 (0.07), 539 (0.09), 557 (0.09), 578 (0.28).

Pd(II) complex of 5-(N-benzyliminomethyl)-2,3,7,8,12,13,17,18-octaethylporphyrin (18): was obtained by the same procedure as for compound **(17)** but with benzylamine. Yield of **(18)** was 35.9 mg (61%). NMR ^{1}H (600 MHz, $CDCl_3$), δ, ppm: 1.59 (6H, t, CH_2-CH_3), 1.88 (6H, t, CH_2-CH_3)1.91-1.94 (12H, m, CH_2-CH_3), 3.46 (2H, s, CH_2Bn), 3.74 (4H, q, CH_2-CH_3), 4.01-4.05 (12H, m, CH_2-CH_3), 7.36-7.39 (1H, m, *C* part of *AA'BB'C* spin system of Ph), 7.44-7.47 (2H, m, *BB'* part of *AA'BB'C* spin system of Ph), 7.65-7.67 (2H, m, *AA'* part of *AA'BB'C* spin system of Ph), 10.02 (1H, s, *meso*-H), 10.06 (2H, s, *meso*-H), 10.99-11.0 (1H, broad m, CH=NBn). HRMS, m/z: 756.3267. Calcd. for $C_{44}H_{52}N_5Pd$ ($[M+H]^+$) 756,3258. UV-Vis (CH_2Cl_2), λ_{max}, nm ($A_{rel.}$): 399 (1.00), 521 (0.03), 553 (0.13).

Ni(II) complex of 5-(N-methyliminomethyl)-2,3,7,8,12,13,17,18-octaethylporphyrin (19) was obtained by the same procedure as for compound **(17)**. Yield of **(19)** was 43.6 mg (82%)**:** NMR ^{1}H (600 MHz, $CDCl_3$), δ, ppm: 1.61 (3H, t, CH_2-CH_3), 1.77-1.84 (18H, m, CH_2-CH_3), 3.70 (4H, q, CH_2-CH_3), 3.84 (3H, d, CH=N-CH_3), 3.85-3.89 (12H, m, CH_2-CH_3) , 9.541 (1H, s, *meso*-H), 9.543 (2H, s, *meso*-H), 10,77 (1H, d, CH=NCH_3). MS (MALDI-TOF), m/z: 632,5369. Calcd. for $C_{38}H_{47}N_5Ni$ ($[M+H]^+$) 633,5282. UV-Vis (CH_2Cl_2), λ_{max}, nm (log ε): 401 (1,00), 530 (0,05), 565 (0,09).

Ni(II) complex of 5-(N-benzyliminomethyl)-2,3,7,8,12,13,17,18-octaethylporphyrin (20): was obtained by the same procedure as for compound **(17)** but with benzylamine. Yield of **(20)** was 48.2 mg (81%). NMR ^{1}H (600 MHz, $CDCl_3$), δ, ppm: 1.60 (6H, t, CH_2-CH_3), 1.77 (6H, t, CH_2-CH_3), 1.80-1.85 (12H, m, CH_2-CH_3), 3.6 (4H, q, CH_2-CH_3), 3.84-3.90 (12H, m, CH_2-CH_3), 4.18 (2H, s, CH_2Bn), 7.29-7.31 (1H, m, *C* part of *AA'BB'C* spin system of Ph), 7.35-7.37 (2H, m, *BB'* part of *AA'BB'C* spin system of Ph), 7.42-7.44 (2H, m, *AA'* part of *AA'BB'C* spin system of Ph), 9.53 (3H, s, *meso*-H), 10.78 (1H, s, CH=NBn). HRMS, m/z: 708.2335. Calcd. for $C_{44}H_{52}N_5Ni$ ($[M+H]^+$) 709.2167. UV-Vis (CH_2Cl_2), λ_{max}, nm ($A_{rel.}$): 401(1.00), 531 (0.04), 576 (0.08).

Thermolysis procedure: Azomethine derivative of complexes **(5)**, **(11)** or **(12)** (0.25 mmol) was heated at 250 °C in vacuum (0.05 mm Hg) for 3 minutes. The products were isolated by preparative TLC with eluents CH_2Cl_2/EtOH 100:1 and 100:4.

Compound (24): Thermolysis of **(5)** yielded yielded 29 mg (13%) of **(24)**. NMR ^{1}H (600 MHz, $CDCl_3$), δ, ppm: 1.23-1.26 (6H, m, CH_2-CH_3), 1.31-1.34 (6H, m, CH_2-CH_3), 2.80 (2H, t, CH_2), 3.02 (2H, m, CH_2), 3.22 (6H, m, β-CH_2, CH_2), 3.39 (3H, s, β-CH_3), 3.47 (3H, s, β-CH_3), 3.52 (3H, s, β-CH_3), 3.79 (2H, m, CH_2), 3.86 (2H, m, CH_2), 4.05 (t, 17^1-CH_2), 4.26-4.29 (12H, m, CH_2), 4.33 (2H, m, 15^1-CH_2), 9.37 (1H, s, *meso*-H), 9.62 (1H, s, *meso*-H), 9.71, (1H, s, *meso*-H). HRMS, m/z: 884.2904. Calcd. for $C_{45}H_{53}N_4O_8Pd$: ($[M+H]^+$) 883.2898. UV-Vis (CH_2Cl_2), λ_{max}, nm ($A_{rel.}$): 396 (1.00), 517 (0.07), 548 (0.17).

Compound (26): Thermolisys of **(5)** yielded yielded 40 mg (19%) of **(26)**. NMR ^{1}H (600 MHz, $CDCl_3$), δ, ppm: 1.17-1.26 (9H, m, CH_2-CH_3), 2.62 (3H, s, NCH_3), 3.19-3.16 (6H, m, CH_2-CH_3), 3.29-3.42 (2H, m, CH_2-lactam cycle), 3.32 (3H, s, β-CH_3), 3.42 (3H, s, β-CH_3), 3.44 (3H, s, β-CH_3), 3.53 (3H, s, β-CH_3), 4.17-4.32 (12H, m, CH_2CH_2CO), 4.78 (1H, m, CH), 7.13 (1H, d, CH), 9.70 (1H, s, *meso*-H), 9.71 (1H, s, *meso*-H), 9.76 (1H, s, *meso*-H). HRMS, m/z: 866.2737. Calcd. for $C_{44}H_{50}N_5O_7Pd$ ($[M+H]^+$) 866.2745. UV-Vis (CH_2Cl_2), λ_{max}, nm ($A_{rel.}$): 395 (1.00), 519 (0.05), 549 (0.17).

Compound (29): Thermolisys of **(11)** yielded 29 mg (14%) of **(29)**.

NMR ^{1}H (600 MHz, $CDCl_3$), δ, ppm: 3.11 (7H, s, CH_2, β-CH_3), 3.21-3.24 (4H, m, CH_2), 3.48 (2H, m, 13^1-CH_2), 3.53 (6H, s, β-CH_3), 3.70 (3H, s, OCH_3), 3.72 (3H, s, OCH_3), 3.74 (3H, s, OCH_3), 3.79 (3H, s, OCH_3), 3.97 (2H, s, CH_2), 4.11 (2H, m, CH_2), 4.23-4.26 (4H, m, CH_2), 4.56 (2H, m, 15^1-CH_2), 9.49 (1H, s, *meso*-H), 9.66 (1H, s, *meso*-H), 9.79, (1H, s, *meso*-H). HRMS, m/z: 827.2264. Calcd. for $C_{41}H_{45}N_4O_8Pd$ ($[M+H]^+$) 827.2272. UV-Vis (CH_2Cl_2), λ_{max}, nm ($A_{rel.}$): 397 (1.00), 514 (0.06), 549 (0.15).

Compound (30): Thermolisys of **(12)** yielded 26 mg (18%) of **(30)**. NMR ^{1}H (600 MHz, $CDCl_3$), δ, ppm: 9.75 (1H, s, *meso*-H), 9.74 (1H, s, *meso*-H), 9.61 (1H, s, *meso*-H), 4.90 (2H, m, 10^1-CH_2), 4.27-4.15 (8H, m, CH_2-CH_3), 3.80 (2H, t, 12^1-CH_2), 3.78 (3H, s, CH_3), 3.73 (3H, s, CH_3), 3.71 (3H, s, CH_3), 3.70 (3H, s, OCH_3), 3.51 (3H, s, OCH_3), 3.50 (3H, s, OCH_3), 3.31 (3H, s, OCH_3), 3.26-3.13 (8H, m, CH_2CH_2CO). HRMS, m/z: 779.2598. Calcd. for $C_{41}H_{45}N_4O_8Ni$ ($[M+H]^+$) 779.2591.

Interaction of azomethine derivatives of porphyrins with bases: A solution of 30 mg (0.04 mmol) of Pd(II) complex of 5-(N-benzyliminomethyl)-2,3,7,8,12,13,17,18-octaethylporphyrin **(18)** in 10 ml DMF was heated to 100 °C and 124 mg (1.1 mmol) of potassium tert-butylate was added. The reaction mixture was stirred for 5 seconds, then the heating was stopped and 25 ml of cold water was added to the mixture. The resulting mixture was extracted with dichloroethane (3 x 50 ml). The organic fraction was dried over Na_2SO_4 and evaporated in vacuum. The products were isolated with preparative TLC in dichloromethane yielding 13 mg (49%) of Pd(II) complex of 5-cyano-2,3,7,8,12,13,17,18-octaethylporphyrin (**44**) and 8.9 mg (34%) of Pd(II) complex of 5-hydroxy-2,3,7,8,12,13,17,18-octaethylporphyrin (**45**). Compounds **(46)**, **(47)**, **(48)** were obtained from the corresponding Ni(II) complexes **(19), (20)** by the same procedure as for **44**, **45.**

Pd(II) complex of 5-cyano-2,3,7,8,12,13,17,18-octaethylporphyrin (44): NMR ^{1}H (600 MHz, $CDCl_3$), δ, ppm: 1.86 (16H, t, CH_2-$\underline{CH_3}$), 1.93 (6H, t, CH_2-$\underline{CH_3}$), 3.91-4.00 (12H, m, $\underline{CH_2}$-CH_3), 4.30 (4H, m, $\underline{CH_2}$-CH_3), 9.89 (1H, s, *meso*-H), 9.90 (2H, s, *meso*-H). HRMS, m/z: 664.2629. Calcd. for $C_{37}H_{44}N_5Pd$: ($[M+H]^+$) 664.2632. UV-Vis (CH_2Cl_2), λ_{max}, nm ($A_{rel.}$): 403 (1.00), 544 (0.05), 575 (0.21).

Pd(II) complex of 5-hydroxy-2,3,7,8,12,13,17,18-octaethylporphyrin (45): HRMS, m/z: 655.2637. Calcd. for $C_{36}H_{45}N_4OPd$ ($[M+H]^+$) 655.2628. UV-Vis (CH_2Cl_2), λ_{max}, nm ($A_{rel.}$):403 (1.00), 517 (0.09), 550 (0.07).

Ni(II) complex of 5-cyano-2,3,7,8,12,13,17,18-octaethylporphyrin (46): NMR ^{1}H (600 MHz, $CDCl_3$), δ, ppm: 1.80 (16H, t, CH_2-$\underline{CH_3}$), 1.87 (6H, t, CH_2-$\underline{CH_3}$), 3.82-3.89 (12H, m, $\underline{CH_2}$-CH_3), 4.19 (4H, q, $\underline{CH_2}$-CH_3), 9.55 (1H, s, *meso*-H), 9.57 (2H, s, *meso*-H). HRMS, m/z: 616.2961. Calcd. for $C_{37}H_{44}N_5Ni$ ($[M+H]^+$) 616.2950. UV-Vis (CH_2Cl_2), λ_{max}, nm ($A_{rel.}$): 406 (1.00), 540 (0.05), 589 (0.7).

Ni(II) complex of 5-hydroxy-2,3,7,8,12,13,17,18-octaethylporphyrin (47): HRMS, m/z: 607.2935. Calcd. for $C_{36}H_{45}N_4ONi$ ($[M+H]^+$) 607.2947. UV-Vis (CH_2Cl_2), λ_{max}, nm ($A_{rel.}$): 413 (1.00), 564 (0.03), 616 (0.02).

Ni(II) complex of 5-(N-methylaminocarbonyl)-2,3,7,8,12,13,17,18-octaethylporphyrin (48): NMR ^{1}H (600 MHz, $CDCl_3$), δ, ppm: 1.80-1.82 (24H, m, CH_2-$\underline{CH_3}$), 3.30 (3H, d, N$\underline{CH_3}$), 3.86-3.90 (16H, m, $\underline{CH_2}$-CH_3), 5.87 (1H, m, NH), 9.60 (1H, s, *meso*-H), 9.64 (2H, s, *meso*-H). HRMS, m/z: 648.3202. Calcd. for $C_{38}H_{48}N_5NiO$ ($[M+H]^+$) 648.3212. UV-Vis (CH_2Cl_2), λ_{max}, nm ($A_{rel.}$): 395 (0.89), 549 (0.06), 556 (0.11).

Ni(II) complex of 5-(aminocarbonyl)-2,3,7,8,12,13,17,18-octaethylporphyrin (50).

NMR ^{1}H (600 MHz, $CDCl_3$), δ, ppm: 1.64 (6H, t, CH_2-$\underline{CH_3}$), 1.79-1.82 (18H, m, CH_2-$\underline{CH_3}$), 3.86-3.93 (16H, m, $\underline{CH_2}$-CH_3), 5.76 (1H, bs, NH), 6.36 (1H, bs, NH), 9.58 (1H, s, *meso*-H), 9.63 (2H, s, *meso*-H). HRMS, m/z: 635.3069. Calcd. for $C_{37}H_{46}N_5NiO$ ($[M+H]^+$) 634.3056. UV-Vis (CH_2Cl_2), λ_{max}, nm ($A_{rel.}$): 394 (1.00), 519 (0.05), 553 (0.13).

5-oxo-2,3,7,8,12,13,17,18-octaethylphlorin (51): A solution of 38 mg (0.063 mmol) of Ni (II) complex of 5-hydroxy-2,3,7,8,12,13,17,18-octaethylporphyrin **(47)** in a mixture of trifluoroacetic acid (10 ml) and concentrated sulfuric acid (1 ml) was stirred at room temperature for 2 minutes, then 50 ml of cold water was added. The resulting mixture was extracted with dichloroethane (3 x 50 ml). The organic fraction was evaporated in vacuum. The product was isolated using a preparative TLC with the eluent CH_2Cl_2/EtOH 100:1 yielding 29.8 mg (86%) of **(51)**. HRMS, m/z: 551.3766. Calcd. for $C_{36}H_{47}N_4O$: ($[M+H]^+$) 551.3750. UV-Vis (CH_2Cl_2), λ_{max}, nm ($A_{rel.}$): 407 (1.00), 550 (0.03) 598 (0.05), 652 (0.10), 705 (0.18).

Supporting Information

X-ray Crystallographic files in CIF format. Crystallographic data for **8**, **25**, **27** and **45** have been deposited with the Cambridge Crystallographic Data Centre as the supplementary publication nos. CCDC 1871457-1871460. Copies of data can be obtained free of charge on application to CCDC, 12 Union Road, Cambridge CB21EZ, UK (fax: (44)1223-336-033; e-mail: deposit@ccdc.cam.ac.uk).

Acknowledgements

We thank ESRF for the access to ID22 station, experiment MA-3313. This research was supported by the Russian Ministry of Science and Education, grant No. RFMEFI61616X0069.

Keywords: porphyrins, Vilsmeier formylation, Schiff bases, thermolysis, annulation

[1] D. B. Papkovsky, T. C. O'Riordan, *J. Fluoresc.* **2005**, *15*, 569–584.
[2] E. D. Sternberg, D. Dolphin, C. Brückner, *Tetrahedron* **1998**, *54*, 4151–4202.
[3] M. Ethirajan, Y. Chen, P. Joshi, R. K. Pandey, *Chem. Soc. Rev.* **2011**, *40*, 340–362.
[4] O. S. Wolfbeis, *J. Mater. Chem.* **2005**, *15*, 2657–2669.
[5] N. A. M. Pereira, M. Laranjo, J. Casalta-Lopes, A. C. Serra, M. Piñeiro, J. Pina, J. S. Seixas de Melo, M. O. Senge, M. F. Botelho, L. Martelo, H. Burrows, E. Pinho, T. Melo., *ACS Med. Chem. Lett.* **2017**, *8*, 310–315.
[6] H. Xiang, L. Zhou, Y. Feng, J. Cheng, D. Wu, X. Zhou, *Inorg. Chem.* **2012**, *51*, 5208–5212.
[7] L. L. Li, E. W. G. Diau, *Chem. Soc. Rev.* **2013**, *42*, 291–304.
[8] X. F. Wang, H. Tamiaki, *Energy Environ. Sci.* **2010**, *3*, 94–106.
[9] J. C. Barona-Castaño, C. C. Carmona-Vargas, T. J. Brocksom, K. T. De Oliveira, M. Graça, P. M. S. Neves, M. Amparo, F. Faustino, *Molecules* **2016**, *21*, 1–27.
[10] Y. Chen, A. Li, Z.-H. Huang, L.-N. Wang, F. Kang, *Nanomaterials* **2016**, *6*, 51.
[11] L. B. Josefsen, R. W. Boyle, *Met. Based. Drugs* **2008**, *2008*, 1–24.
[12] C. Peng, Y. Li, H. Liang, J. Cheng, Q. Li, X. Sun, Z. Li, F. Wang, Y. Guo, Z. Tian, L.Yang, Y.Tian, Z. Zhang, W. Cao, *J. Photochem. Photobiol. B Biol.* **2011**, *102*, 26–31.
[13] M. Vicente, K. Smith, *Curr. Org. Synth.* **2014**, *11*, 3–28.
[14] J. S. Lindsey, *Chem. Rev.* **2015**, *115*, 6534–6620.
[15] S. Richeter, C. Jeandon, J. P. Gisselbrecht, R. Graff, R. Ruppert, H. J. Callot, *Inorg. Chem.* **2004**, *43*, 251–263.
[16] B. D. P. Arnold, R. Gaete-holmes, A. W. Johnson, A. R. P. Smith, A. Geoffrey, *J. Chem. Soc. Perkin Trans. 1* **1978**, 1660–1670.
[17] A. K. Burrell, D. L. Officer, *Synlett* **1998**, 1297–1307.
[18] H. J. Callot, *Tetrahedron* **1973**, *29*, 899–901.
[19] D. P. Arnold, A. W. Johnson, M. Mailvaganam, *J. Chem. Soc. Perkin Trans. 1* **1976**, 366–370.
[20] F.-P. Montforts, G. Scheurich, A. Meier, G. Haake, F. Höper, *Tetrahedron Lett.* **1991**, *32*, 3477–3480.
[21] S. Runge, M. O. Senge, I. Chemic, O. Chemic, F. U. Berlin, D.-Berlin, *Tetrahedron* **1999**, *55*, 10375–10390.
[22] M. Graça, H. Vicente, K. M. Smith, *J. Org. Chem.* **1991**, *56*, 4407–4418.
[23] G. V. Ponomarev, *Chem. Heterocycl. Comp.* **1996**, *32*, 1263–1280.
[24] G. V. Ponomarev, Y. V. Morozova, D. V. Yashunsky, *Chem. Heterocycl. Compd.* **2001**, *37*, 277–279.
[25] L. Jaquinod, D. J. Nurco, C. J. Medforth, R. K. Pandey, T. P. Forsyth, M. M. Olmstead, K. M. Smith, *Angew. Chem.* **1996**, *35*, 1013–1016.
[26] A. W. Johnson, D. Oldfield, *J. Chem. Soc.* **1966**, 794–798.
[27] L. Witte, F. Jiirgen-Hinrich, *Angew. Chem.* **1975**, *14*, 361–363.
[28] D. Papkovsky, C. Cork, *Sensor material and uses thereof to simultaneously sense two analytes, US 2011/0236986 A1*, **2011**.
[29] I. V Sazanovich, A. Balakumar, K. Muthukumaran, E. Hindin, C. Kirmaier, J. R. Diers, J. S. Lindsey, D. F. Bocian, D. Holten, *Inorg. Chem.* **2003**, *42*, 6616–6628.
[30] A. Zieleniewska, S. R. Harper, D. P. Arnold, D. M. Guldi, *Chem. - A Eur. J.* **2018**, *24*, 3058–3067.
[31] B. Temelli, O. Y. Ozasik, *Eur. J. Org. Chem.* **2017**, *2017*, 4905–4915.
[32] T. E. O. Screen, I. M. Blake, L. H. Rees, W. Clegg, J. Borwick, H. L. Anderson, *J. Chem. Soc., Perkin Trans. 1* **2002**, 320–329.
[33] A. N. Volov, I. A. Zamilatskov, I. S. Mikhel, D. R. Erzina, G. V. Ponomarev, O. I. Koifman, A. Y. Tsivadze, *Macroheterocycles* **2014**, *7*, 256–261.
[34] V. S. Tyurin, D. R. Erzina, I. A. Zamilatskov, A. Y. Chernyadiev, G. V. Ponomarev, D. V. Yashunskiy, A. V. Maksimova, K. V. Neverov, A. S. Kozlov, A. A. Krasnovsky, A. Yu.Tsivadze, *Macroheterocycles* **2015**, *8*, 376–383.
[35] G. V. Ponomarev, A. M. Shul'ga, B. V. Rozynov, *Chem. Heterocycl. Compd.* **1993**, *29*, 155–162.
[36] G. V. Ponomarev, B. V. Rozynov, *Chem. Heterocycl. Compd.* **1975**, *9*, 1065–1068.
[37] Y. V Morozova, D. V Yashunsky, B. I. Maksimov, G. V Ponomarev, *Chem. Heterocycl. Compd.* **2003**, *39*, 434–435.
[38] G. V. Ponomarev, D. V. Yashunskii, A. S. Moskovkin, *Chem. Heterocycl. Compd.* **1997**, *33*, 324–328.
[39] P. S. Clezy, C. L. Lim, J. S. Shannon, *Aust. J. Chem.* **1974**, *27*, 2431–2437.
[40] R. Persch, H. Budzikiewicz, *Heterocycles* **1976**, *5*, 749–770.
[41] G. V. Ponomarev, V. P. Suboch, A. N. Lyashko, *Chem. Heterocycl. Compd.* **1978**, *14*, 631–636.
[42] R. S. Czernuszewicz, *J. Porphyr. Phthalocyanines* **2000**, *4*, 426–431.
[43] D. M. Quizon-Colquitt, T. D. Lash, *J. Heterocycl. Chem.* **1993**, *30*, 477–482.
[44] I. A. Zamilatskov, E. V. Savinkina, A. N. Volov, M. S. Grigoriev, I. S. Lonin, L. N. Obolenskaya, G. V. Ponomarev, O. I. Koifman, A. S. Kuzovlev, G. M. Kuzmicheva, A. Yu.Tsivadze, *Macroheterocycles* **2012**, *5*, 308–314.
[45] A. O. Shkirdova, I. A. Zamilatskov, N. M. Stanetskaya, V. A. Tafeenko, V. S. Tyurin, V. V. Chernyshev, G. V. Ponomarev, A. Yu.

Tsivadze, *Macroheterocycles* **2017**, *10*, 480–486.

[46] D. R. Erzina, I. A. Zamilatskov, N. M. Kurochkina, G. V. Ponomarev, V. A. Tafeenko, *Acta Crystallogr., Sect. C: Struct. Chem.* **2017**, *73*, 68–71.

[47] M. O. Senge, G. V. Ponomarev, T. P. Forsyth, K. M. Smith, *Zeitschrift für Naturforsch. B* **1996**, *51*, 1644–1648.

[48] X.-Q. Gu, W. Chen, D. Morales-Morales, C. M. Jensen, *J. Mol. Catal. A: Chem.* **2002**, *189*, 119–124.

[49] N. Barooah, C. Tamuly, J. B. Baruah, *J. Chem. Sci.* **2005**, *117*, 117–122.

[50] K. D. M. Harris, M. Tremayne, P. Lightfoot, P. G. Bruce, *J. Am. Chem. Soc.* **1994**, *116*, 3543–3547.

[51] V. Chernyshev, *Russ. Chem. Bull.* **2001**, *50*, 2273–2292.

[52] H. Tsue, M. Horiguchi, R. Tamura, K. Fujii, H. Uekusa, *J. Synth. Org. Chem. Jpn.* **2007**, *65*, 1203–1212.

[53] W. I. F. David, K. Shankland, *Acta Crystallogr. Sect. A Found. Crystallogr.* **2008**, *64*, 52–64.

[54] K. D. M. Harris, in *Advanced X-Ray Crystallography*, *Top. Curr. Chem. 315* (Ed.:K.Rissanen), Springer-Verlag, Berlin Heidelberg **2012**, pp. 133–178.

[55] A. N. Fitch, *J. Res. Natl. Inst. Stand. Technol.* **2004**, *109*, 133–142.

[56] P. E. Werner, L. Eriksson, M. Westdahl, *J. Appl. Crystallogr.* **1985**, *18*, 367–370.

[57] J. W. Visser, *J. Appl. Crystallogr.* **1969**, *2*, 89–95.

[58] V. B. Zlokazov, *Comput. Phys. Commun.* **1995**, *85*, 415–422.

[59] G. S. Pawley, *J. Appl. Crystallogr.* **1981**, *14*, 357–361.

[60] S. G. Zhukov, V. V. Chernyshev, *Zeitschrift für Krist.* **2001**, *216*, 5–9.

[61] S. V. Andreev, S. A. Zverev, I. A. Zamilatskov, N. M. Kurochkina, G. V. Ponomarev, A. N. Fitch, V. V. Chernyshev, *Acta Crystallogr. Sect. C Struct. Chem.* **2017**, *73*, 47–51.

[62] I. S. Lonin, E. S. Belyaev, A. Y. Tsivadze, G. V. Ponomarev, N. N. Lonina, A. N. Fitch, V. V. Chernyshev, *Macroheterocycles* **2017**, *10*, 474–479.

[63] V. B. Zlokazov, V. V. Chernyshev, *J. Appl. Crystallogr.* **1992**, *25*, 447–451.

[64] H. Toraya, *J. Appl. Crystallogr.* **1986**, *19*, 440–447.

[65] W. A. Dollase, *J. Appl. Crystallogr.* **1986**, *19*, 267–272.

[66] N. C. Popa, *J. Appl. Crystallogr.* **1998**, *31*, 176–180.

[67] C. R. Groom, F. H. Allen, *Angew. Chem.* **2014**, *53*, 662–671.

[68] A. B. Cairns, A. L. Goodwin, *Chem. Soc. Rev.* **2013**, *42*, 4881–4893.

[69] V. A. Tafeenko, S. I. Gurskiy, *Cryst. Growth Des.* **2016**, *16*, 940–945.

[70] T. D. Brennan, W. R. Scheidt, J. A. Shelnutt, *J. Am. Chem. Soc.* **1988**, *110*, 3919–3924.

[71] A. D. Becke, *J. Chem. Phys.* **1993**, *98*, 5648–5652.

[72] C. Lee, W. Yang, R. G. Parr, *Phys. Rev. B* **1988**, *37*, 785–789.

[73] M. J. Frisch, G. W. Trucks, H. B. Schlegel, G. E. Scuseria, M. A. Robb, J. R. Cheeseman, J. A. Montgomery, Jr., T. Vreven, K. N. Kudin, J. C. Burant, J. M. Millam, S. S. Iyengar, J. Tomasi, V. Barone, B. Mennucci, M. Cossi, G. Scalmani, N. Rega, G. A. Petersson, H. Nakatsuji, M. Hada, M. Ehara, K. Toyota, R. Fukuda, J. Hasegawa, M. Ishida, T. Nakajima, Y. Honda, O. Kitao, H. Nakai, M. Klene, X. Li, J. E. Knox, H. P. Hratchian, J. B. Cross, V. Bakken, C. Adamo, J. Jaramillo, R. Gomperts, R. E. Stratmann, O. Yazyev, A. J. Austin, R. Cammi, C. Pomelli, J. W. Ochterski, P. Y. Ayala, K. Morokuma, G. A. Voth, P. Salvador, J. J. Dannenberg, V. G. Zakrzewski, S. Dapprich, A. D. Daniels, M. C. Strain, O. Farkas, D. K. Malick, A. D. Rabuck, K. Raghavachari, J. B. Foresman, J. V. Ortiz, Q. Cui A. G. Baboul, S. Clifford, J. Cioslowski, B. B. Stefanov, G. Liu, A. Liashenko, P. Piskorz, I. Komaromi, R. L. Martin, D. J. Fox, T. Keith, M. A. Al-Laham, C. Y. Peng, A. Nanayakkara, M. Challacombe, P. M. W. Gill, B. Johnson, W. Chen, M. W. Wong, C. Gonzalez, J. A. Pople, Gaussian 03, Revision E. 01, Gaussian, Inc., Wallingford CT, **2004**.

[74] J. H. Fuhrhop, S. Besecke, J. Subramanian, C. Mengersen, D. Riesner, *J. Am. Chem. Soc.* **1975**, *97*, 7141–7152.