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Exploring replacement of axially coordinated ligands in ruthenium(II) phthalocyaninates

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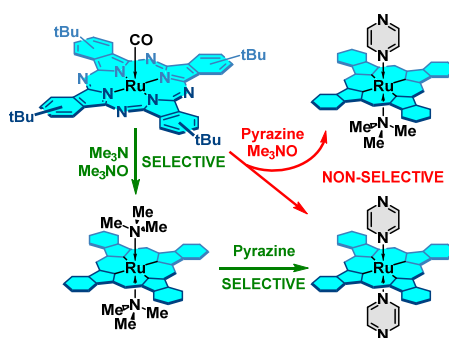
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Abstract:

We report an extensive study of axial ligand replacement in ruthenium(II) complexes with tetra-*tert*-butyl-phthalocyanine (tBu₄Pc). For this purpose oxidative decarbonylation of [tBu₄PcRu](CO) in the presence of trimethylamine was performed providing [tBu₄PcRu](NMe₃)₂ complex in 92% yield. Its heating with pyrazine in *o*-dichlorobenzene at 100°C gave [tBu₄PcRu](Pyz)₂ in quantitative yield. A simplified TD-DFT approximation has been used to explain the difference in the appearance of UV–Vis spectra of synthesized complexes with different N-donor ligands in terms of π - π^* or charge transfer excitations, assignment was validated by the studies of solvatochromism of synthesized complexes. The reported finding can pave a convenient way to a relatively mild selective synthesis of ruthenium phthalocyaninates carrying N-donor aromatic ligands. Such complexes attract interest for various photo- and electroactive applications, catalysis and medicine.

Keywords: ruthenium; phthalocyanine; decarbonylation; axial ligands replacement; simplified TD-DFT

1. Introduction

Ruthenium phthalocyaninates (RuPcs) possess unique properties valuable for different applications [1]. These complexes demonstrate nonlinear optical behavior [2], ability to generate singlet oxygen under light irradiation, providing cell death which is used in photodynamic therapy (PDT) [3–8]. Due to their light-harvesting properties, RuPcs can be used as triplet injectors [9] and charge collectors [10] in organic

solar cells. The binuclear complex $(\text{RuPc})_2$ has uncommonly high conductivity and triplet configuration with the magnetic moment which can vary upon deposition on different surfaces in spintronic nano-devices [11–14]. Coordination abilities of these complexes ensure their application as components of sensors [15–17]. RuPcs can also act as heterogeneous [18] and homogeneous [11,19–21] catalysts for oxidation processes; there're also examples of catalytic activity in carbene transfer reactions [22–24].

Ruthenium phthalocyaninates can be synthesized either by template condensation of phthalonitriles [25,26] or via direct interaction of phthalocyanines with ruthenium sources [27–29]. Typically, the products of such reactions contain strongly coordinated σ -donor/ π -acceptor carbonyl ligand at one of axial positions – $\text{Pc}^*\text{Ru}(\text{CO})$ [1] (Hereinafter Pc^* stands for both unsubstituted and substituted phthalocyanine macrocycles).

Replacement of carbonyl ligand with various N-donor ligands L, mainly pyridine derivatives, paves the way to PcRuL_2 as moieties of multicomponent systems, such as water-soluble non-aggregating PDT agents [7], photocatalysts for water decomposition [29] and trifluoromethylation reactions [30], supramolecular 2D ensembles in Langmuir monolayers [31], ensembles with efficient photoinduced electron transfer [32] or coordination polymers with wide range of conductivity characteristics [33]. Thus, preparation of ruthenium phthalocyaninates with axially coordinated N-donor ligands is an important task, but their synthesis typically cannot be performed by a simple replacement of strongly bound carbonyl group – the reaction of $\text{Pc}^*\text{Ru}(\text{CO})$ complexes with pyridine derivatives L results in the formation of heteroligand complex $\text{Pc}^*\text{Ru}(\text{CO})\text{L}$ [32,34]. In contrast to CO ligand, the N-donor ligand in such complexes is bound relatively weakly and can be readily replaced with other concurrent molecules. On the contrary, the symmetric complexes Pc^*RuL_2 are much more resistant to ligand exchange.

So, in order to prepare the stable complexes Pc^*RuL_2 one of the following methods can be used:

(i) the template condensation of phthalonitrile in the presence of ruthenium source and N-donor ligand [10,30,35–39];

(ii) the replacement of labile benzonitrile molecules in $\text{Pc}^*\text{Ru}(\text{PhCN})_2$ by substituted pyridine ligands at 25-70°C [4,5,7,34,40]. The starting complexes can be prepared either by template condensation of phthalonitriles with $\text{RuCl}_3 \cdot n\text{H}_2\text{O}$ [3] or by direct metalation of phthalocyanines with ruthenium carbonyl, $\text{Ru}_3(\text{CO})_{12}$ in benzonitrile [4,40]. In the latter case short-time reflux leads to carbonyl complexes Pc^*RuCO [20] whereas overnight reflux of reaction mixture leads to ruthenium complexes with coordinated benzonitrile molecules in two axial positions $\text{Pc}^*\text{Ru}(\text{PhCN})_2$ [4];

(iii) the substitution of labile acetonitrile molecules in $\text{Pc}^*\text{Ru}(\text{CH}_3\text{CN})_2$ by substituted pyridine ligands at 25-80°C. The starting complexes can be synthesized from $\text{Pc}^*\text{Ru}(\text{CO})$ via decarbonylation under UV-irradiation in acetonitrile solution [5,7,32]. There are also two examples of direct substitution of carbonyl ligand under UV-irradiation with pyridine but the yields were moderate [41,42];

(iv) the replacement of other N-donor ligands is performed under harsher conditions in comparison with nitrile ligands. Thus, there are single examples of substitution of axially coordinated ammonia (190°C) [35], pyridine (130°C) [10] or picoline (160°C) [43] with less volatile substituted pyridine ligands.

(v) the use of trimethylamine oxide, Me_3NO as a reagent for oxidative decarbonylation of $\text{Pc}^*\text{Ru}(\text{CO})$ in the presence of aromatic or aliphatic N-donor ligands in refluxing chloroform. This method is characterized by mild conditions and relatively high yields of target complexes [44–46], although it can be complicated by formation of side products – heteroligand complexes with axially coordinated trimethylamine and N-donor ligand. In some cases these by-products could be isolated in moderate yields [44]. However, when ruthenium(II) tetra-15-crown-5-phthalocyaninate with axially coordinated pyrazine (Pyz) molecules $[(15\text{C}5)_4\text{PcRu}](\text{Pyz})_2$ was synthesized using this method, it could not be separated from the side complex $[(15\text{C}5)_4\text{PcRu}](\text{Pyz})(\text{NMe}_3)$ [2]. To overcome this problem, the obtained mixture of the target symmetrical complex $[(15\text{C}5)_4\text{PcRu}](\text{Pyz})_2$ and heteroligand by-product $[(15\text{C}5)_4\text{PcRu}](\text{Pyz})(\text{NMe}_3)$ was refluxed in *o*-dichlorobenzene (*o*-DCB, b.p. 180°C) in the presence of an excess of pyrazine, which replaced volatile trimethylamine under high-temperature conditions. Although this additional step ensured a product purity and a high total yield, it required the repetitive use of ligand in excess, which may be inconvenient if less available N-donor compounds should be used.

In the present work we further investigate the trimethylamine replacement to showcase the advantages of this leaving ligand in the synthesis of ruthenium phthalocyaninates bearing axially coordinated N-donor ligands. With this aim we prepared a novel ruthenium(II) tetra-*tert*-butylphthalocyaninate with axial coordinated trimethylamine molecules $[\text{tBu}_4\text{PcRu}](\text{NMe}_3)_2$ in high yields from the carbonyl complex $[\text{tBu}_4\text{PcRu}](\text{CO})$ by optimization of the previously reported oxidative decarbonylation protocol using Me_3NO . We demonstrated that the complex could undergo a quantitative replacement of Me_3N ligands with pyrazine molecules under short-time reflux in *o*-DCB, (b.p. 180°C). Moreover, the quantitative replacement of trimethylamine with pyrazine can be still accomplished at even lower temperature (100°C).

2. Experimental

2.1. Materials and methods

Chloroform (stabilized with 0.6-1% EtOH) was distilled from K_2CO_3 to remove acidic impurities. Chloroform, which was used as a solvent in reactions, was additionally filtered through a layer of alumina. Me_3NO was recrystallized from DMF. Solution of Me_3N in N-methyl-2-pyrrolidone ($\text{Me}_3\text{N}^*\text{NMP}$) was prepared by slow addition a saturated aqueous solution of NMe_3^*HCl to a solid alkali; the resulting gas was passed through a trap with solid alkali and condensed in the graduated tube cooled with ice and salt. Condensed trimethylamine (3 ml) was diluted with NMP to get 100 ml of 0.34 M solution. Tetra-2(3),9(10),16(17),23(24)-*tert*-butyl-phthalocyaninoruthenium(II) carbonyl $[\text{tBu}_4\text{PcRu}](\text{CO})$, was synthesized according to the previously reported procedure [28].

High-resolution mass spectra were recorded on Bruker maXis tandem quadrupole/time-of-flight mass analyzer, equipped with an ESI source, acetonitrile was used as the solvent for the samples. MALDI-TOF mass spectra were measured on a Bruker Daltonics Ultraflex mass spectrometer in positive ion mode with 2,5-dihydroxybenzoic acid (DHB) as a matrix. Samples of complexes were dissolved in chloroform, mixed with matrix solution in methanol, and dripped onto a stainless steel target. UV–Vis absorption spectra were measured on JASCO V-770 spectrometer in the 250-900 nm range in rectangular

quartz cells with optical pathway of 10 mm using CHCl_3 as a solvent. FT-IR spectra were measured using a JASCO FT/IR-6600 spectrometer with ATR PRO ONE Technologies accessory with a diamond crystal PKS-D1F in the range $4000\text{--}250\text{ cm}^{-1}$. ^1H NMR spectra were acquired on a Bruker Avance 600 spectrometer. Samples were prepared in CDCl_3 (Cambridge Isotope Laboratories, Inc.), which was filtered through a layer of alumina prior to use. NMR spectra were referenced to the solvent signals [47].

2.2. Synthesis

2.2.1. Bis-trimethylamine [tetra-tert-butyl-phthalocyaninato]ruthenium(II), $[\text{tBu}_4\text{PcRu}](\text{NMe}_3)_2$

Method A: The mixture of $[\text{tBu}_4\text{PcRu}](\text{CO})$ (12.2 mg, $14.1\text{ }\mu\text{mol}$) and Me_3NO (3.8 mg, $281.7\text{ }\mu\text{mol}$) was dissolved in chloroform (3.5 mL) in 25 ml single-neck flask, equipped with the reflux condenser. The mixture was degassed by three-time pumping and flushing with argon on the Schlenk line. Then, the mixture was refluxed for 3h, until the Q-bands of starting $[\text{tBu}_4\text{PcRu}](\text{CO})$ (651 nm) vanished in the UV-Vis spectrum of the reaction mixture sample and the Q-band of $[\text{tBu}_4\text{PcRu}](\text{NMe}_3)_2$ complex appeared (627 nm). After cooling to room temperature, chloroform was removed at reduced pressure and then the mixture was suspended in water (30 ml) under sonication. The resulting blue precipitate was filtered through a syringe filter ($45\text{ }\mu\text{m}$), washed three times with water and washed off the filter with CHCl_3 . Then, the compound was isolated by size-exclusion chromatography on BioBeads SX-1 gel in $\text{CHCl}_3 + 2.5\text{ vol.}\%$ MeOH, affording pure complex $[\text{tBu}_4\text{PcRu}](\text{NMe}_3)_2$ (4.1 mg, 30 %) as dark-blue solid.

Method B: The mixture of $[\text{tBu}_4\text{PcRu}](\text{CO})$ (56.3 mg, $65\text{ }\mu\text{mol}$), Me_3NO (19.5 mg, $260\text{ }\mu\text{mol}$) and $\text{Me}_3\text{N}^*\text{NMP}$ solution (3 ml) was dissolved in chloroform (5 mL) in 25 ml two-neck flask, equipped with the reflux condenser. The mixture was degassed by three-time pumping and flushing with argon on the Schlenk line. Then, the mixture was stirred at $50\text{ }^\circ\text{C}$. The reaction was monitored by UV-Vis spectroscopy until the Q-bands of starting $[\text{tBu}_4\text{PcRu}](\text{CO})$ (651 nm) vanished in the UV-Vis spectra of the reaction mixture samples and the Q-band of $[\text{tBu}_4\text{PcRu}](\text{NMe}_3)_2$ complex appeared (627 nm). After 1 h, the reaction was stopped and chloroform was removed at reduced pressure. Then the mixture was poured into water (25 ml), the resulting blue precipitate was filtered through a syringe filter ($22\text{ }\mu\text{m}$), washed three times with water and washed off the filter with CHCl_3 . Then, the compound was isolated by size-exclusion chromatography on BioBeads SX-1 gel in $\text{CHCl}_3 + 2.5\text{ vol.}\%$ MeOH, affording pure complex $[\text{tBu}_4\text{PcRu}](\text{NMe}_3)_2$ (57.4 mg, 92 %) as dark-blue solid. UV-Vis in CHCl_3 , λ_{max} , nm (log ϵ): 627 (4.87), 579 sh. (4.43), 380 (4.39), 316 (5.08). ^1H NMR (600 MHz, CDCl_3) δ ppm: 9.25-9.21 (m, 4H, $\text{H}_{\text{Pc}2}$), 9.13-9.07 (m, 4H, $\text{H}_{\text{Pc}3}$), 8.00-7.97 (m, 4H, $\text{H}_{\text{Pc}1}$), 1.79-1.78 (m, 36H, H_{tBu}), -2.25 (s, 18H, $\text{H}_{\text{Me}3\text{N}}$). MALDI TOF MS, m/z: found 1675.7 - $[\text{M}-2\text{NMe}_3]_2^+$, calculated for $[\text{C}_{96}\text{H}_{96}\text{N}_{16}\text{Ru}_2]^+$ - 1676.6. HR-ESI, m/z: found - 956.4553 - $[\text{M}]^+$, calculated for $[\text{C}_{54}\text{H}_{66}\text{N}_{10}\text{Ru}]^+$ - 956.4524. FT-IR, $\nu\text{ cm}^{-1}$: 2952 (s), 2922 (s), 2854 (s), 1726 (m), 1614 (w), 1491 (s), 1464 (s), 1394 (m), 1363 (m), 1317 (m), 1257 (s), 1192 (w), 1149 (4), 1126 (s), 1051 (w), 941 (w), 895 (w), 829 (m), 760 (m), 694 (w), 671 (w), 532 (w).

2.2.2. Bis-pyrazine [tetra-tert-butyl-phthalocyaninato]ruthenium(II), $[\text{tBu}_4\text{PcRu}](\text{Pyz})_2$

Method A: The mixture of $[\text{tBu}_4\text{PcRu}](\text{CO})$ (29 mg, $33.5\text{ }\mu\text{mol}$), Me_3NO (10 mg, $133.9\text{ }\mu\text{mol}$) and pyrazine (134 mg, $1675\text{ }\mu\text{mol}$) was dissolved in chloroform (5 ml) in 25 ml two-neck flask, equipped

with the reflux condenser. The mixture was degassed by three-time pumping and flushing with argon on the Schlenk line and refluxed. The reaction was monitored by UV–Vis spectroscopy until the Q-bands of starting $[\text{tBu}_4\text{PcRu}](\text{CO})$ (651 nm) vanished in the UV–Vis spectra of the reaction mixture samples and the Q-band of $[\text{tBu}_4\text{PcRu}](\text{Pyz})_2$ complex appeared (647 nm). After 1 h, the reaction was stopped. Chloroform and pyrazine were removed at reduced pressure. According to ^1H NMR spectroscopy, the resulting mixture (33.5 mg) contained target $[\text{tBu}_4\text{PcRu}](\text{Pyz})_2$ and side-forming $[\text{tBu}_4\text{PcRu}](\text{NMe}_3)(\text{Pyz})$ complexes in the molar ratio 9:1. This mixture and pyrazine (134 mg, 1.7 mmol) were dissolved in *o*-DCB (3 ml) in 10 ml flask, solution was degassed by three-time pumping and flushing with argon on the Schlenk line and refluxed for 20 min under a slow argon flow. After cooling to ambient temperature, *o*-DCB and pyrazine was removed at reduced pressure. The subsequent purification by size-exclusion chromatography on BioBeads SX-1 gel in $\text{CHCl}_3 + 2.5 \text{ vol.}\% \text{ MeOH}$, affording pure dark-blue complex $[\text{tBu}_4\text{PcRu}](\text{Pyz})_2$ (31.6 mg, 95%).

Method B: The mixture of $[\text{tBu}_4\text{PcRu}](\text{NMe}_3)_2$ (19 mg, 19.9 μmol) and pyrazine (79.5 mg, 1 mmol) was dissolved in *o*-DCB (3 ml) in 10 ml flask. The mixture was degassed by three-time pumping and flushing with argon on the Schlenk line and refluxed for 20 min under a slow stream of argon. After cooling to ambient temperature, *o*-DCB and pyrazine was removed at reduced pressure. The subsequent purification by size-exclusion chromatography on BioBeads SX-1 gel in $\text{CHCl}_3 + 2.5 \text{ vol.}\% \text{ MeOH}$, affording pure dark blue complex $[\text{tBu}_4\text{PcRu}](\text{Pyz})_2$ (18.8 mg, 95%). UV–Vis in CHCl_3 , λ_{max} , nm (log ϵ): 647 (4.80), 588 (4.47), 449 (3.99), 315 (4.97). ^1H NMR (600 MHz, CDCl_3) δ ppm: 9.27-9.24 (m, 4H, $\text{H}_{\text{Pc}2}$), 9.16-9.11 (m, 4H, $\text{H}_{\text{Pc}3}$), 8.04-8.02 (m, 4H, $\text{H}_{\text{Pc}1}$), 6.44 (d, $J = 3.5 \text{ Hz}$, 4H, $\text{H}_{\text{Pyz}2}$), 2.41 (d, $J = 3.5 \text{ Hz}$, 4H, $\text{H}_{\text{Pyz}1}$), 1.77-1.75 (m, 36H, H_{tBu}). MALDI TOF MS, m/z : found 1675.7 – $[\text{M}-2\text{Pyz}]_2^+$, calculated for $[\text{C}_{96}\text{H}_{96}\text{N}_{16}\text{Ru}_2]^+ - 1676.6$. FT–IR, $\nu \text{ cm}^{-1}$: 2954 (s), 2924 (s), 2862 (m), 1732 (w), 1614 (w), 1583 (m), 1493 (s), 1415 (m), 1394 (m), 1363 (m), 1317 (m), 1281 (m), 1257 (m), 1192 (w), 1153 (s), 1128 (s), 1051 (m), 1016 (w), 941 (w), 895 (w), 831 (w), 804 (w), 758 (w), 694 (w), 669 (w), 631 (w).

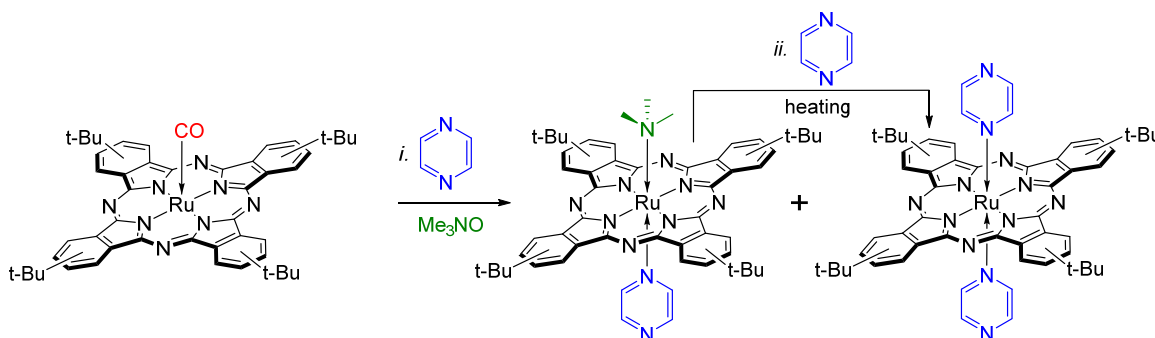
2.3. Computational details

Quantum calculations were performed using ORCA 5.0.0 [48]. Geometry optimization of the molecules was performed in gas phase via DFT using the BP86 functional, def2-TZVP basis set for light atoms and def2-ECP effective core potential for ruthenium [49]. Vertical excitation energies were evaluated after the geometry optimization by performing simplified time-dependent (sTD-DFT) [50,51] calculations using range-separated functional CAM-B3LYP [52], def2-TZVP basis set for light atoms and def2-ECP effective core potential for ruthenium.

3. Results and discussion

With the aim to compare different methods of decarbonylation based on using Me_3NO we started with the synthesis of the complex $[\text{tBu}_4\text{PcRu}](\text{Pyz})_2$ by previously reported protocol [2], using reaction of $[\text{tBu}_4\text{PcRu}](\text{CO})$ with Me_3NO in the presence of pyrazine excess (Scheme 1*i*). This ligand was chosen because of its ditopic nature with the possibility of its subsequent modification [8] or formation of conducting coordination polymers with shish-kebab architecture [53–55].

According to UV–Vis spectra, decarbonylation of $[\text{tBu}_4\text{PcRu}](\text{CO})$ resulted in the slight bathochromic shift of the Q-band from 651 nm to 647 nm and appearance of a new band at 449 nm (**Fig. 1**). The $^1\text{H-NMR}$ spectrum of the final reaction mixture showed the presence of the target *homoligand* complex $[\text{tBu}_4\text{PcRu}](\text{Pyz})_2$ and the side *heteroligand* complex with coordinated molecule of trimethylamine $[\text{tBu}_4\text{PcRu}](\text{NMe}_3)(\text{Pyz})$ in molar ratio 9:1 (**Fig. S1**). This mixture turned out to be inseparable, thus at the following step we refluxed it with an excess of pyrazine in *o*-DCB under a flow of argon to substitute volatile trimethylamine in ruthenium coordination sphere with pyrazine (**Scheme 1ii**). Altogether this two-step procedure afforded pure $[\text{tBu}_4\text{PcRu}](\text{Pyz})_2$ complex in high yield (95%).



Scheme 1. Two-step synthesis of the complex $[\text{tBu}_4\text{PcRu}](\text{Pyz})_2$ by *i.* – oxidative decarbonylation in the presence of pyrazine leading to $[\text{tBu}_4\text{PcRu}](\text{Pyz})_2$ contaminated with inseparable $[\text{tBu}_4\text{PcRu}](\text{Pyz})(\text{NMe}_3)$ and *ii.* – replacement of trimethylamine, leading to pure $[\text{tBu}_4\text{PcRu}](\text{Pyz})_2$.

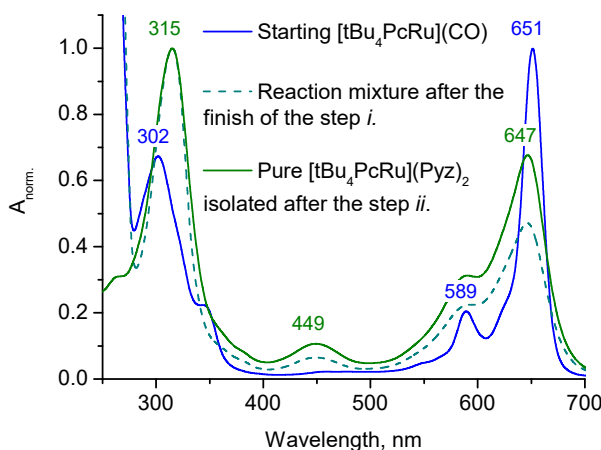


Fig. 1. UV–Vis spectra in CHCl_3 of the reaction mixture containing $[\text{tBu}_4\text{PcRu}](\text{CO})$, pyrazine and Me_3NO at the beginning and after the end of reaction and pure $[\text{tBu}_4\text{PcRu}](\text{Pyz})_2$.

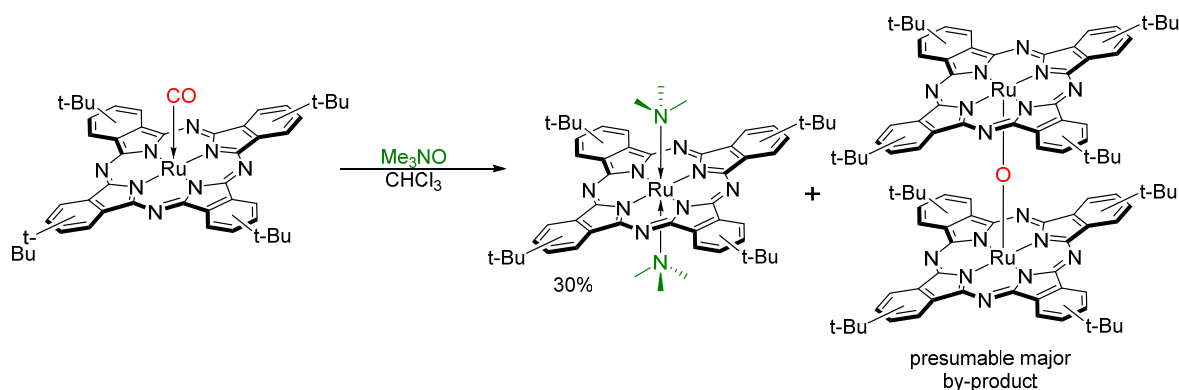
The absence of coordinated trimethylamine and purity of the resulting complex was confirmed by $^1\text{H-NMR}$ spectroscopy (**Fig. S2**), which showed characteristic up-field shifted signals at 6.44 and 2.41 ppm corresponding to two axially coordinated pyrazine molecules. This NMR spectrum together with the FT-IR (**Fig. S3**) and UV–Vis spectra (**Figs. 1 and S4**) were consistent with previously reported data for $[\text{tBu}_4\text{PcRu}](\text{Pyz})_2$ [37].

The obtained result suggests that trimethylamine ligand can act as a leaving group in the synthesis of ruthenium phthalocyaninates with other N-donor ligands. To study the advances of this finding, we decided to synthesize $[\text{tBu}_4\text{PcRu}](\text{NMe}_3)_2$ as a precursor for complexes with other ligands.

With this aim, carbonyl-containing complex was treated with trimethylamine oxide alone, which can perform the oxidative decarbonylation and serve as a source of trimethylamine at same time [46].

Thus, we treated $[\text{tBu}_4\text{PcRu}](\text{CO})$ with a twenty-fold excess of Me_3NO in refluxing chloroform which led to the mixture of target ruthenium phthalocyaninate $[\text{tBu}_4\text{PcRu}](\text{NMe}_3)_2$ and a new side product (Scheme 2). The separation of these compounds by size-exclusion chromatography on Bio-Beads SX-1 revealed that the complex with axially coordinated trimethylamine molecules isolated in a 30 % yield has the essentially longer retention time.

Although the product with the shorter retention time had the same Q-band as $[\text{tBu}_4\text{PcRu}](\text{NMe}_3)_2$, the general appearance of its UV–Vis spectrum was different. For example, the band at 380 nm was present only in the spectrum of complex with trimethylamine (Fig. 2). The ^1H NMR spectrum of this side-forming compound also showed the absence of coordinated trimethylamine molecules. In the MALDI TOF spectrum we detected the molecular ion peak with $m/z = 1693.1$, which may be attributed to the μ -oxo-dimeric ruthenium(III) complex $[\text{tBu}_4\text{PcRu}]_2(\mu\text{-O})$ (calc. $m/z = 1692.6$), the presumed by-product of this reaction. We suppose that it can be formed via the oxidation of ruthenium(II) phthalocyanine $[\text{tBu}_4\text{PcRu}](\text{CO})$ with trimethylamine oxide. Similarly, ruthenium(II) porphyrinates $\text{PorRu}(\text{CO})$ can be oxidized by pyridine- [56] or 2,6-dichloropyridine-N-oxides [57] to form oxo-species.



Scheme 2. Reaction of the complex $[\text{tBu}_4\text{PcRu}](\text{CO})$ with an excess of trimethylaminoxide.

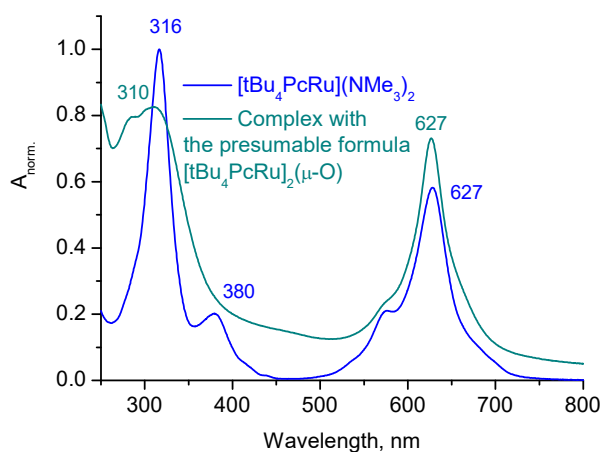
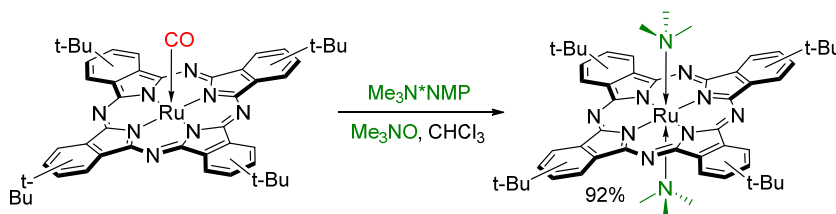


Fig. 2. UV–Vis spectra of isolated complexes in CHCl_3 : the complex $[\text{tBu}_4\text{PcRu}](\text{NMe}_3)_2$ and the side-forming product with presumable formula $[\text{tBu}_4\text{PcRu}]_2(\mu\text{-O})$.

To prevent the formation of μ -oxo-species, we decided to use Me_3NO only as a decarbonylating reagent, while a 0.34 M solution of trimethylamine in N-methyl-2-pyrrolidone ($\text{NMe}_3 \cdot \text{NMP}$) was used as a source of N-donor ligands. Thus, these reagents allow to carry out the reaction under mild conditions (50°C , CHCl_3), and chromatographic purification afforded the complex $[\text{tBu}_4\text{PcRu}](\text{NMe}_3)_2$ in excellent yield of 92% (Scheme 3). Reaction was monitored by UV–Vis spectroscopy: the spectra of reaction

mixture showed complete disappearance of the characteristic Q-band [tBu₄PcRu](CO) at 651 nm and appearance of Q-band of [tBu₄PcRu](NMe₃)₂ at 627 nm.



Scheme 3. Improved method of synthesis of the complex [tBu₄PcRu](NMe₃)₂.

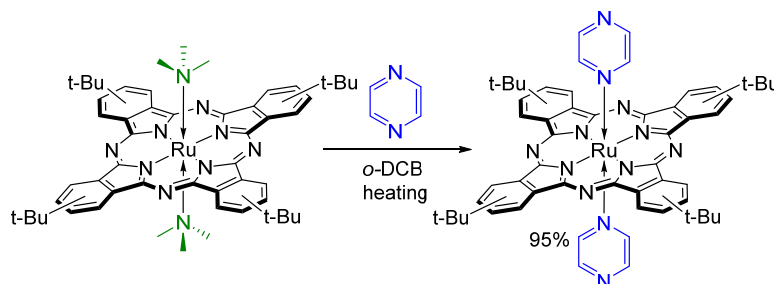
The ¹H NMR spectrum of the complex [tBu₄PcRu](NMe₃)₂ (Fig. S5) showed a singlet in the up-field region at $\delta = -2.25$ ppm, attributed to protons of methyl groups in two axially coordinated trimethylamine molecules. Note that the signal of the NMe₃ group in the heteroligand complex [tBu₄PcRu](Pyz)(NMe₃) is shifted downfield to -2.04 ppm (Figure S1) which allowed us to identify the aforementioned side product in reactions of oxidative decarbonylation.

The FT-IR spectroscopy has also confirmed decarbonylation due to the vanishing of CO stretching band at 1951 cm⁻¹ (Figure S6). The UV-Vis spectrum of the complex (Figures 2 and S7) was consistent with the appearance of spectra of ruthenium phthalocyaninates bearing N-donor axial ligands [44–46].

Importantly, the MALDI-TOF mass spectroscopy was not suitable for characterization of [tBu₄PcRu](Pyz)(NMe₃) as its spectrum showed only the peak of dimeric species [tBu₄PcRu]₂⁺ (Figure S8). Their formation was presumably induced by laser irradiation of [tBu₄PcRu](Pyz)(NMe₃) with removal of axially coordinated ligand and subsequent dimerization of the formed RuPc species [58]. In principle, other ionization methods like fast bombardment atom, field desorption [59] or electrospray ionization (ESI) [5,7,28,34] can be used to avoid the elimination of axial ligands. In our case, the HR-ESI mass spectrometry allowed to observe the molecular ions [tBu₄PcRu](NMe₃)₂⁺ with *m/z* values and isotopic distribution in agreement with the calculated values (Figure S9).

To check the applicability of this complex as a precursor for the synthesis of ruthenium phthalocyaninates with axially coordinated N-donor ligands, we performed its reaction with pyrazine (Scheme 4). At room temperature no ligand exchange was observed. However, when this mixture was refluxed in *o*-DCB for 20 min, volatile trimethylamine was removed from the ruthenium coordination sphere and the complex with two coordinated pyrazine molecules was formed. In the process of ligand substitution, we observed the characteristic bathochromic shift of Q-band from 627 nm to 647 nm in agreement with the spectra of individual compounds (Figures 1 and 2). The complex [tBu₄PcRu](Pyz)₂ was isolated in 95% yield after evaporation of solvent and pyrazine under reduced pressure and chromatographic purification on Bio-Beads SX-1 sorbent. The spectral characteristics of the isolated complex matched those obtained during decarbonylation of [tBu₄PcRu](CO) in the presence of pyrazine. The mechanism of this replacement is likely to include thermal dissociation of Ru-NMe₃ bond with subsequent coordination of pyrazine. Previously, such mechanism was suggested to describe replacement of phosphine and phosphite ligands coordinated to PcRu with 1-methylimidazole and pyridine [60].

In order to explore the possibility of NMe₃ replacement in starting complex under milder conditions, we have estimated at which lower temperature the ligand exchange still occurs. To that end, the reaction between [tBu₄PcRu](NMe₃)₂ and pyrazine in chlorobenzene was performed under 100 °C. It was demonstrated that reaction was completed after 6 h of heating. The complete replacement of trimethylamine ligands with pyrazine was also evidenced by ¹H NMR spectrum of the reaction mixture. Thus, this finding can be used for the synthesis of complexes with more fragile ligands which might not withstand refluxing in *o*-DCB.



Scheme 4. Reaction of [tBu₄PcRu](NMe₃)₂ with an excess of pyrazine.

To explain the observed difference between the UV–Vis spectra of complexes with axially coordinated NMe₃ and Pyz, we used simplified time-dependent density functional theory approach (sTD-DFT). This method was previously shown to afford orders of magnitude speedup of the calculations in comparison to the full TD-DFT approach and in most cases provides even more accurate predictions of vertical excitation energies [51,61,62]. With this aim we first optimized geometries of [tBu₄PcRu](NMe₃)₂ and [tBu₄PcRu](Pyz)₂ with BP86 functional, triple- ζ def2-TZVP basis set for light elements and def2-ECP effective core potential for ruthenium, and then performed sTD-DFT calculations using range-separated hybrid functional CAM-B3LYP and the same basis sets in ORCA 5.0.0 package.

Comparison of geometries of complexes evidenced the notably longer Ru–NMe₃ bond of 2.239 Å compared to Ru–N_{Pyz} bond of 2.089 Å. These values are in excellent agreement with X-ray data for Ru–N bonds observed in ruthenium(II) crown-phthalocyaninates with axially coordinated tertiary aliphatic amine 1,4-diazabicyclo[2.2.2]octane (2.244(3) Å) [45] and pyrazine (2.089(4) Å) [2]. The shortening of the bond between Ru and aromatic ligand comes from π -back-bonding which can be the reason of the higher stability of this complex, providing the possibility of the ligand replacement.

The sTD-DFT calculations showed that the Q-band of the complex with NMe₃ should be shifted hypsochromically by 0.07 eV in comparison with Pyz-containing complex, which is also in agreement with the experimentally observed hypsochromic shift of 0.06 eV (Fig. 3). In both cases Q-bands correspond to excitations between Pc-centered HOMO and pair of LUMOs – the famous Gouterman orbitals (Figs. S10 and S11, Tables S1 and S2).

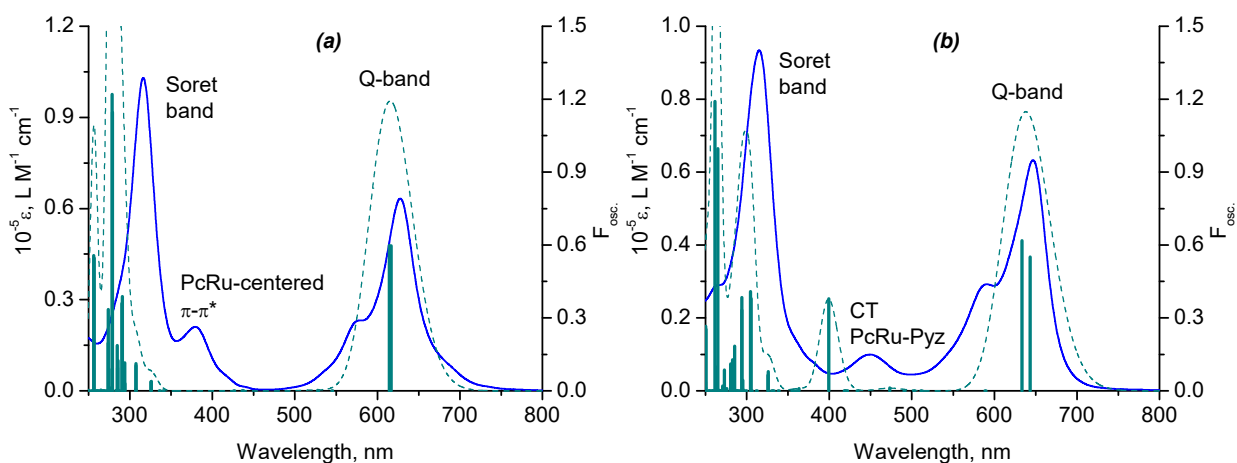


Fig. 3. Comparison of experimental and predicted UV-Vis spectra of $[\text{tBu}_4\text{PcRu}](\text{NMe}_3)_2$ – (a) and $[\text{tBu}_4\text{PcRu}](\text{Pyz})_2$ – (b). Vertical bars show positions and oscillator strengths of predicted vertical excitations, dashed lines show the shapes of calculated spectra with 0.1 eV half-width.

As for the high-energy bands at the foot of the Soret band, the sTD-DFT calculations suggest that in the case of $[\text{tBu}_4\text{PcRu}](\text{NMe}_3)_2$ the excitations which give rise to the weak band at 380 nm correspond to complicated configurational interaction between orbitals, localized solely on RuPc part of the molecule (Table S1). The observed overestimation of energies of transitions forming the Soret band envelopes is a common drawback of sTD-DFT method inherited from the full TD-DFT [63].

Different situation is observed in the case of $[\text{tBu}_4\text{PcRu}](\text{Pyz})_2$. The calculations suggest that the band at 449 nm corresponds to excitation from HOMO-1 to LUMO+2 (predicted position – 398 nm). Here HOMO-1 is mainly composed of Pc-centered π -orbital and ruthenium d_{yz} orbital, while LUMO+2 is pyrazine-based π^* -orbital, thus this band can be attributed to charge transfer from PcRu to Pyz ligands (Fig. 4, Table S2).

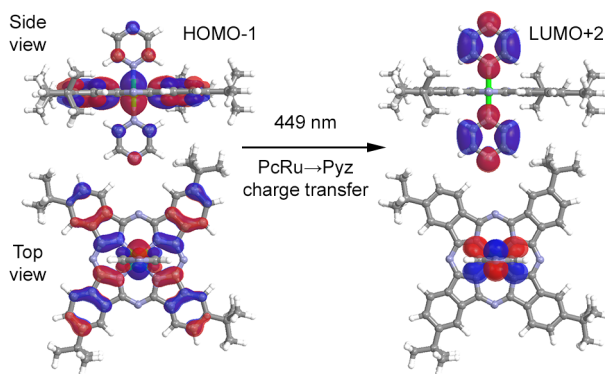


Fig. 4. Molecular orbitals responsible for the appearance of the charge-transfer band in UV-Vis spectrum of $[\text{tBu}_4\text{PcRu}](\text{Pyz})_2$ according to sTD-DFT calculations.

To verify the assignment of the discussed bands either to π - π^* or CT excitations, we checked solvatochromic behavior of these complexes comparing their UV-Vis spectra in chloroform and acetone as solvents with sufficiently different dielectric constants, dipolar moments, refractive indices, etc. As expected, the most prominent solvatochromic effect was observed for the CT band in spectra of $[\text{tBu}_4\text{PcRu}](\text{Pyz})_2$ while it was quite small for π - π^* transitions including Q-bands in spectra of both complexes (Fig. 5). Similar strong solvatochromic shifts of intramolecular CT bands were reported previously on the examples of carbazole-substituted phthalocyanines [64] whereas the Q-bands of these

and other phthalocyanines showed only modest response to change of the solvent nature [65,66]. The interest in biorelevant molecules possessing solvatochromic behavior as environment-sensitive probes [67] justifies the need in further study of this class of complexes.

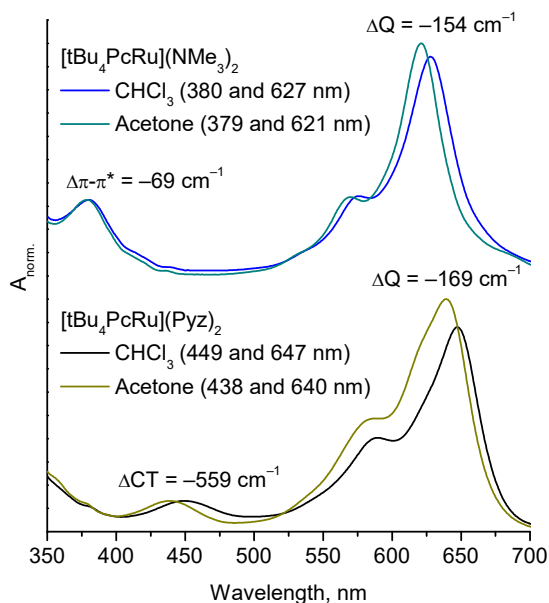


Fig. 5. UV–Vis spectra of $[t\text{Bu}_4\text{PcRu}](\text{NMe}_3)_2$ and $[t\text{Bu}_4\text{PcRu}](\text{Pyz})_2$ in acetone and chloroform. Values in brackets indicate the positions of bands in corresponding spectra. Intensities of spectra are normalized to optical densities of the considered π - π^* and CT bands respectively.

4. Conclusions

In the present work we have contributed to studies of coordination chemistry of ruthenium phthalocyaninates in the context of axial ligand replacement on the examples of ruthenium(II) tetra-*tert*-butyl-phthalocyaninates with axially coordinated carbonyl, trimethylamine and pyrazine ligands. We showed that oxidative decarbonylation of $[t\text{Bu}_4\text{PcRu}](\text{CO})$ in the presence of either Me_3NO alone or Me_3NO with pyrazine was not selective, yielding mixtures of various products. However, treatment of carbonyl complex with Me_3NO and trimethylamine in *N*-methyl-2-pyrrolidone selectively yielded $[t\text{Bu}_4\text{PcRu}](\text{NMe}_3)_2$, whose NMe_3 groups could be quantitatively replaced with aromatic pyrazine ligands under relatively mild conditions. From this viewpoint, ruthenium phthalocyaninates bearing σ -donor aliphatic amines can be considered as convenient precursors for synthesis of complexes with σ -donor/ π -acceptor aromatic ligands. The optical properties of these complexes, important for their practical application, can be interpreted using a simplified TD-DFT approach, and, in principle, the same method can be used to directionally design new complexes with given functional characteristics.

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performed using the equipment of CKP FMI IPCE RAS and IGIC RAS. HR-ESI measurements were measured in N.D. Zelinsky Institute of Organic Chemistry RAS.

Appendix A. Supplementary data

Supplementary data to this article can be found online at <https://doi.org/...>

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