# Novel Rhodium Porphyrin Derivatives.
# III. Synthesis and Characterization of Rhodium(III) Porphyrinates in Solution of Alkyl Amides

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## Abstract

Amino and alkylrhodium derivatives of *meso*-tetraphenylporphyrin ($H_2TPP$) and octaethylporphyrin ($H_2OEP$) have been synthesized by reacting the macrocycles with hydrated rhodium trichloride in different alkyl amides.

No substantial difference in the reactivity of the two porphyrins has been observed.

Possible reaction pathways correlating the nature of the products with the steric hindrance of the solvents are discussed.

## Introduction

Rhodium porphyrin derivatives have been extensively studied because of their possible applications as models for biological systems and their activity as catalysts in some organic reactions [1–12].

Thus a large number of Rh(I) and Rh(III) porphyrinates have been prepared by reacting $[Rh(CO)_2Cl]_2$ and the appropriate macrocycles in non-coordinating solvents [13–15].

The use of *N,N*-dimethylformamide (DMF) as a solvent for the metallation reaction of porphyrins can be regarded as a standard procedure [16] but highly reactive metals, such as rhodium, may lead to the formation of several different complexes. Thus Gouterman *et al.* [17] observed decarboxylation of the solvent and incorporation of *N,N*-dimethylamine (DMA) in the resulting metal complex $[RhEP(DMA)_2Cl]$ (EP = etioporphyrin I).

In recent papers [18, 19] we have described the highly reproducible reactions between hydrated rhodium trichloride and $H_2TPP$ or $H_2OEP$ in pure DMF.

The difference in electronic and steric effects between $H_2TPP$ and $H_2OEP$ is quite remarkable since the two HOMOs ($a_{1u}$ and $a_{2u}$) in the macrocycles $\pi$ system are reversed between the two compounds [20].

This paper reports on the comparison of the reactivity of $H_2TPP$ and $H_2OEP$ with hydrated rhodium trichloride in *N,N*-dimethylacetamide (DMAc), *N*-methylformamide (MMF), *N*-ethylformamide (MEF) and *N,N*-diethylformamide (DEF).

## Experimental

IR spectra were recorded on a Perkin Elmer Mod. 983 spectrophotometer as nujol mulls. NMR spectra were recorded on a Bruker WP 80 SY instrument as $CDCl_3$ solutions with tetramethylsilane (TMS) as internal standard. Electronic spectra were recorded on a Perkin-Elmer Lambda 9 spectrophotometer as dichloromethane solutions. All solvents were reagent grade and were used with no further purification. $H_2TPP$ and $H_2OEP$ were synthesized according to literature procedures [21]. Octaethylporphyrin was further purified by column chromatography on silica gel eluting with chloroform/n-hexane 1:1 and recrystallization from chloroform/methanol 1:2.

### *Synthesis of [RhTPP(DMA)Cl]*

$H_2TPP$ (500 mg) and $RhCl_3 \cdot xH_2O$ (500 mg) were dissolved in DMAc (250 ml) and kept at 150 °C, under nitrogen, for 18 h. The solvent was removed under vacuum and the residue was chromatographed on silica gel. $[CH_3RhTPP]$ was obtained by elution with chloroform (yield: 10%), whilst [RhTPP(DMA)Cl] was eluted with chloroform/methanol 98:2 and recrystallized from chloroform–methanol 1:2 (yield was higher than 50%).

(Dimethylamino)*meso*-tetraphenylporphyrinato rhodium(III) chloride can be obtained by warming [RhTPPCl] (200 mg) in DMF (100 ml), under nitrogen, at 120 °C, for 18 h. Yield: 70%.

### *Synthesis of [EtRhTPP]*

$H_2TPP$ (500 mg) and $RhCl_3 \cdot xH_2O$ (500 mg) were dissolved in DEF (250 ml) and kept at 150 °C, under nitrogen, for 24 h. The solvent was removed under

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vacuum and the residue was chromatographed on silica gel eluting with chloroform/n-hexane 60:40. The complex was obtained by evaporating the eluted fractions and recrystallizing from dichloromethane/n-hexane 1:3. The yield was always higher than 75%.

The same product was obtained by warming under nitrogen at 150 °C a solution of [RhTPPCl] in DEF for 18 h.

*Synthesis of [RhTPP(MMA)₂X] Complexes (X = [Rh(CO)₂Cl₂]⁻, Cl⁻)*

$H_2TPP$ (500 mg) and $RhCl_3 \cdot xH_2O$ (500 mg) were dissolved in MMF (250 ml) and kept at 150 °C, under nitrogen, for 1 h. The reaction mixture was diluted with water (500 ml) and extracted with dichloromethane. The organic solution was washed with water and brine. The solvent was removed under vacuum and the residue was chromatographed on silica gel eluting with chloroform/methanol 98:2. Recrystallization from chloroform/n-hexane 1:3 afforded pure $[RhTPP(MMA)_2]^+[Rh(CO)_2Cl_2]^-$. The yield was about 70%.

When the reaction time is prolonged for 24 h the same purification procedure leads to the isolation of $[RhTPP(MMA)_2Cl]$ with the same yield.

*Synthesis of [RhTPP(MEA)₂Cl]*

$H_2TPP$ (500 mg) and $RhCl_3 \cdot xH_2O$ (500 mg) were dissolved in MEF (250 ml) and kept at 150 °C, under nitrogen, for 24 h. The solution was diluted with water (500 ml) and extracted with chloroform. The organic layer was washed with water and brine and evaporated under vacuum. The residue was chromatographed on silica gel eluting with chloroform/methanol 97:3. Recrystallization from chloroform/diethyl ether/n-hexane 1:2:2 afforded the pure product. Yield: 70%.

The same complex was obtained by warming [RhTPPCl] (200 mg) in MEF (100 ml) at 100 °C, under nitrogen, for 6 h. Yield: 70%.

*Synthesis of [RhOEP(DMA)Cl]*

$H_2OEP$ (500 mg) and $RhCl_3 \cdot xH_2O$ (500 mg) were dissolved in DMAc (300 ml) and kept at 150 °C, under nitrogen, for 5 days. The solvent was evaporated under vacuum and the residue chromatographed on silica gel eluting with chloroform until all the unreacted ligand was separated. The complex was then eluted with chloroform/methanol 95:5. Recrystallization from chloroform/n-hexane 1:3 afforded the pure product. Yield: 25%.

*Synthesis of [EtRhOEP]*

$H_2OEP$ (500 mg) and $RhCl_3 \cdot xH_2O$ (500 mg) were dissolved in DEF (250 ml) and kept at 150 °C, under nitrogen, for 24 h. The solvent was removed under vacuum and the residue chromatographed on silica gel eluting with chloroform/n-hexane 60:40. Recrystallization from chloroform/n-hexane 1:3 afforded pure product. Yield: 30%.

*Synthesis of [RhOEP(MMA)₂Cl]*

$H_2OEP$ (500 mg) and $RhCl_3 \cdot xH_2O$ (500 mg) were dissolved in MMF (250 ml) and kept at 150 °C, under nitrogen, for 2 h. The solution was diluted with water (500 ml) and extracted with dichloromethane. The organic layer was washed with water and brine, evaporated and chromatographed on silica gel. Elution with chloroform/methanol 95:5 afforded the product which was recrystallized from chloroform/n-hexane 1:3. Yield: 40%.

*Synthesis of [RhOEP(MEA)₂Cl]*

$H_2OEP$ (500 mg) and $RhCl_3 \cdot xH_2O$ (500 mg) were dissolved in MEF (250 ml) and kept at 150 °C, under nitrogen, for 24 h. The solution was diluted with water (500 ml) and extracted with chloroform. The organic layer was washed with water and brine and evaporated under vacuum. The residue was chromatographed on silica gel eluting with chloroform until all the unreacted porphyrin was separated. The product was then eluted with chloroform/methanol 90:10 and recrystallized from chloroform/n-hexane 1:3. Yield: 20%.

## Results and Discussion

Hydrated rhodium trichloride reacts with porphyrins in DMAc, MMF, MEF and DEF leading to the formation of penta- or hexacoordinated complexes depending on the nature of the amide. Thus, in the same experimental conditions, $H_2TPP$ and $H_2OEP$ react in *N,N*-dimethylacetamide to give [RhTPP(DMA)Cl] and [RhOEP(DMA)Cl]. The tetraphenylporphyrin derivative has been previously obtained by Kadish and coworkers [22] in DMF as an intermediate in the synthesis of $[RhTPP(DMA)_2Cl]$.

If *N*-methylformamide is used as solvent, the reaction rate is higher for both porphyrins and, after few hours, $[RhP(MMA)_2X]$ (MMA = mono-methylamine $X = [Rh(CO)_2Cl_2]^-$ if P = TPP; $X = Cl^-$ if P = OEP) complexes have been isolated. If the reaction is prolonged up to 24 h the tetraphenylporphyrin derivative isolated was found to be $[RhTPP(MMA)_2Cl]$.

When the reaction is carried out in *N*-ethylformamide the products are again the corresponding bisamino derivatives $[RhP(MEA)_2Cl]$ (MEA = monoethylamine; P = TPP, OEP).

Finally, in *N,N*-diethylformamide, $H_2TPP$ and $H_2OEP$ react to give the corresponding ethylrhodium porphyrinates previously obtained by other authors by reaction of porphyrinate rhodium(III) chloride with ethyllithium [23, 24].

TABLE I. Analytical Data for [$RhPL_nX$] Complexes

| P | L | *n* | X | C(%) | | H(%) | | N(%) | |
|---|---|---|---|---|---|---|---|---|---|
| | | | | calc. | found | calc. | found | calc. | found |
| TPP | $CH_3NH_2$ | 2 | Cl | 68.10 | 67.48 | 4.45 | 4.61 | 10.35 | 10.23 |
| TPP | $CH_3NH_2$ | 2 | $Rh(CO)_2Cl_2$ | 57.35 | 57.24 | 3.60 | 3.74 | 8.35 | 8.03 |
| TPP | $CH_3CH_2NH_2$ | 2 | Cl | 68.55 | 67.85 | 5.05 | 4.93 | 10.00 | 10.21 |
| OEP | $(CH_3)_2NH$ | 1 | Cl | 63.75 | 63.42 | 7.20 | 6.96 | 9.80 | 10.28 |
| OEP | $CH_3NH_2$ | 2 | Cl | 61.40 | 61.74 | 7.20 | 7.24 | 11.50 | 11.86 |
| OEP | $CH_3CH_2NH_2$ | 2 | Cl | 63.10 | 63.40 | 7.70 | 7.45 | 11.05 | 11.28 |

TABLE II. Spectral Properties for [$RhPL_nX$] Complexes

| P | L | *n* | X | $\lambda_{max}$ (nm) | NMR | | |
|---|---|---|---|---|---|---|---|
| | | | | | $L_{CH_3}$ | $L_{CH_2}$ | $L_{NH}$ |
| TPP | $CH_3NH_2$ | 2 | Cl | 422, 532, 566 | −3.25t<br>$J = 6$ Hz | | −4.58m |
| TPP | $CH_3NH_2$ | 2 | $Rh(CO)_2Cl_2$ | 422, 532, 566 | −3.35t<br>$J = 6$ Hz | | −4.79m |
| TPP | $CH_3CH_2NH_2$ | 2 | Cl | 424, 532, 566 | −1.71t<br>$J = 7$ Hz | −3.46m | −4.58m |
| OEP | $(CH_3)_2NH$ | 1 | Cl | 406, 520, 552 | −3.54d<br>$J = 7$ Hz | | −6.23m |
| OEP | $CH_3NH_2$ | 2 | Cl | 400, 516, 548 | −3.71t<br>$J = 6$ Hz | | −5.68m |
| OEP | $CH_3CH_2NH_2$ | 2 | Cl | 400, 518, 548 | −1.99t<br>$J = 6$ Hz | −4.02m | −5.69m |

Although the reactions carried out with TPP give products with much higher yields than those performed with OEP, the two porphyrins lead always to the formation of analogous complexes. The similarity in reactivity patterns for these electronically extreme types of macrocycles confirms the observations of Wayland *et al.* [24] and indicates that the variation of the electronic properties caused by substitutent effects results in only minor changes at the metal center.

In order to elucidate the reaction mechanism, [RhTPPCl] has been reacted with DMF, MEF and DEF. All the reactions follow the same pathway of those performed with the metal free porphyrin and hydrated $RhCl_3$ and lead to the formation of the above described derivatives. These results seem to indicate that the decarboxylation of the solvent is subsequent to the metallation of the macrocycle.

It seems in fact reasonable to assume that the transition state involves coordination, through the nitrogen atom, of one or two amide molecules on the rhodium porphyrinate. The reaction can then follow two different pathways both involving the cleavage of a nitrogen–carbon bond in the amide ligand.

In the first case decarboxylation occurs and the resulting product is an amino derivative. A possible mechanism can involve intramolecular hydrogen transfer from the carbon atom to the nitrogen. The formation of the bis-amino derivatives and the reaction rates can then be correlated to the steric hindrance of the amides used as solvents. Thus, in MMF the reaction rate is higher than in DEF or DMF and the products are the bis-amino complexes; with DMAc, which has a higher steric hindrance, only mono-amino derivatives are formed.

The second possible pathway leads to alkylation of the metal probably through migration of an alkyl group from the nitrogen to the rhodium atom. Thus, with DEF, the most hindered species, we have isolated only ethylrhodium porphyrinates.

All complexes have been characterized through elemental analyses, IR and NMR spectra. Analytical data and spectral properties of the newly synthesized products are reported in Tables I and II.

$^1H$ NMR spectra do not show any remarkable feature: all the diagnostic resonances of the axial ligands show a strong upfield shift due to the macrocycle ring current [25]. The shielding effect of the porphyrin is responsible for the inversion of the chemical shifts of the methylenic and methyl proton resonances in the spectra of the ethylamino and alkylrhodium derivatives.

The methyl groups of both TPP and OEP monomethylamino derivatives appear as triplets at $-3.25$ and $-3.71$ ppm respectively. Double resonance experiments proved them to be coupled with the nitrogen bound protons.

The NH stretching appears as a broad band centered around 3300 $cm^{-1}$ in the IR spectra of all complexes. This may be due to the presence of hydrogen bonding between the amine hydrogens and the chloride counter ion. Hydrogen bonds have been indeed reported [17] to be the major intramolecular forces in the crystal structure of bis-(dimethylamine)etio(I)porphyrinato rhodium(III) chloride.

The stretching frequencies of the carbonyl and of the rhodium–chloride groups, the only other diagnostic infrared absorptions, fall in the range usually observed for similar complexes [18, 26–29].

Electronic spectra show the typical hypso character of rhodium(III) porphyrinates [30]: the metal $d^6$ shell seems to be rather inert to the effects of the fifth or sixth ligands.

Further investigation on the mechanism of such reactions are in progress.

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