Novel Rhodium Porphyrin Derivatives IV. A Study of the Interaction between Rhodium Porphyrinates and Amides

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Synthetic metalloporphyrins enjoy continuing popularity as models for metalloenzymes, oxygen transport and biological electron transport systems [1–7].

Although porphyrin metallation in solution has been widely studied, variations of the reaction conditions may lead to different complexes [8].

For instance, the metallation of etio-porphyrin I with hydrated rhodium trichloride in *N,N*-dimethylformamide (DMF) causes decomposition of the solvent and affords the bis-dimethylamino metal derivative [9].

In a recent paper [10] we have described the reactions between hydrated rhodium trichloride and *meso*-tetraphenyl-(H_2TPP) and octaethylporphyrin (H_2OEP) in different alkyl amides and correlated the reaction rates and the nature of the products to the steric hindrance of the solvents.

The purpose of the present work was to investigate the reaction mechanism, employing new amides, with different lengths of the alkyl chains bound to the nitrogen or to the carbon atom.

The reactions were carried out in *N,N*-diethylacetamide (DEAc), *N,N*-diethylpropionamide (DEP), *N*-methylacetamide (NMAc), *N,N*-dipropylformamide (DPF) and *N,N*-diethylformamide (DEF).

Experimental

IR spectra were recorded on a Perkin-Elmer model 983 spectrophotometer as nujol mulls. NMR spectra were recorded on a Bruker WP 80 SY instrument as $CHCl_3$ solutions with tetramethylsilane (TMS) as internal standard. Electronic spectra were recorded on a Perkin-Elmer Lambda 9 spectrophotometer as dichloromethane solutions.

Gas chromatographic analyses were performed on a Carlo Erba HRGC 5300 gas chromatograph equipped with a Supelco 60/80 Carbosieve G, 5′ × 1/8″ SS column (col. temp. 145 to 195 °C at 6 °C/min and hold 5 min; flow rate 50 ml/min N_2; detector FID).

All solvents were reagent grade and were used without further purification. H_2TPP, [TPPRhCl], DEP and DPF were synthesized according to the literature procedure [11, 12].

Synthesis of [TPPRh($COCH_3$)]

H_2TPP (300 mg) and $RhCl_3 \cdot xH_2O$ (300 mg) were dissolved in DEAc (100 ml) and kept at 160 °C under nitrogen, for 18 h. The solvent was evaporated under vacuum and the residue was chromatographed on silica gel eluting with chloroform/n-hexane 1:1.

[TPPRh(CH_3)] was obtained with the first fraction (yield 10%). The second fraction contained [TPPRh($COCH_3$)] which was purified by recrystallization from dichloromethane/n-hexane 1:2 (yield 60%). The same complexes were obtained with identical yields by warming [TPPRhCl] (100 mg) in DEAc (100 ml) under nitrogen at 160 °C, for 3 h.

The pure acetyl derivative was converted to [TPPRh(CH_3)] when kept at 150 °C in DEAc under nitrogen for 8 h.

Synthesis of [RhTPP($COCH_2CH_3$)]

H_2TPP (300 mg) and $RhCl_3 \cdot xH_2O$ (300 mg) were dissolved in DEP (100 ml) and kept at 150 °C for 24 h. The solvent was removed under vacuum and the residue was chromatographed on silica gel eluting with chloroform/n-hexane 1:1. Recrystallization from chloroform/n-hexane 1:2 afforded the pure product (yield 60%).

The same complex was obtained by warming [TPPRhCl] (100 mg) in DEP (100 ml) under nitrogen for 3 h (yield 50%).

Synthesis of [TPPRh(NH_2CH_3)Cl]

H_2TPP (300 mg) and $RhCl_3 \cdot xH_2O$ (300 mg) were dissolved in melted MMAc (100 g) and kept at 180 °C for 24 h. The reaction mixture was diluted with water (500 ml) and extracted with chloroform. The organic solution was washed twice with water and then with brine. The solvent was removed and the residue was chromatographed on silica gel eluting with chloroform. Recrystallization from chloroform/methanol 1:2 afforded the pure product (yield 50%).

The same complex was obtained by warming [TPPRhCl] (100 mg) in MMAc (100 ml) at 100 °C under nitrogen for 24 h (yield 40%).

Synthesis of [TPPRh($NH_2CH_2CH_3$)Cl]

[TPPRhCl] (100 mg) was dissolved in DEF and kept at 80 °C under nitrogen in a sealed vial for 6 h. The reaction gases were examined on a gas chromato-

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graphic column (see above) showing the presence of ethylene. The reaction mixture was evaporated under vacuum and chromatographed on silica gel eluting with chloroform. Recrystallization from dichloromethane/n-hexane 1:2 afforded the pure product (yield 70%).

When the temperature was raised to 150 °C and the reaction time prolonged to 24 h [TPPRh(CH_2-CH_3)] was isolated in good yield [10]. Attempts to convert the amino complex to the ethylrhodium derivative by heating it in other high-boiling solvents such as chlorobenzene were unsuccessful.

Synthesis of {*TPPRh[NH(CH_2CH_3)$_2$]Cl*}

[TPPRhCl] (100 mg) was dissolved in toluene (50 ml) and diethylamine (1 ml) was added. The solution was irradiated with a 200 W halogen lamp for 6 h. The reaction mixture was evaporated and chromatographed on silica gel eluting with chloroform. Recrystallization from dichloromethane/n-hexane 1:2 afforded the pure product (yield 75%).

Results and Discussion

Hydrated rhodium trichloride reacts with *meso*-tetraphenylporphyrin in DEAc, DEP and MMAc, leading to the formation of pentacoordinated complexes.

As we have previously observed in the case of *N,N*-dimethylformamide [10], the same complexes can be obtained by reaction of [TPPRhCl] with amides. Thus it has been confirmed that the first step of the formation of such complexes is the metallation of the macrocyclic ring.

In diethylacetamide the products isolated were [TPPRh($COCH_3$)], previously obtained in two steps by James and Stynes [13], and [TPPRhCH_3]. The latter compound was also obtained by warming the pure acetyl complex in high-boiling solvent (chlorobenzene). It seems conceivable that the formation of the methylrhodium derivative occurs through decarbonylation of the parent acetyl complex.

When the reaction was carried out in diethylpropionamide, the tetraphenyl porphyrin derivative obtained was again an acylrhodium complex; [TPPRh-($COCH_2CH_3$)].

If *N*-methylacetamide was used as solvent, the complex isolated was the mono-amino derivative [TPPRh(NH_2CH_3)Cl].

In dipropylformamide decomposition of the porphyrin was observed at 150 °C while no reaction occurs at lower temperatures.

Using *N,N*-dialkylformamides as solvents, only amino derivatives were obtained [10], indicating that the reactions proceed through coordination of the nitrogen atom.

All these complexes can be then considered as derived from decomposition of the amide used as solvent and addition of an acyl- or amino-fragment to rhodium porphyrinato. The choice between nitrogen or carbon substitution at the metal in the final products seems to be related to the steric hindrance on the nitrogen atom of the amide. In fact, when a highly hindered species, such as *N,N*-dipropylformamide, was used no reaction occurred.

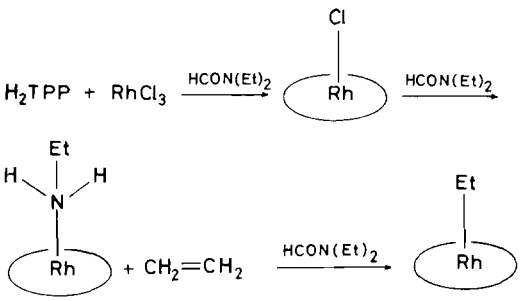
We have previously reported [10] that [TPPRh-(CH_2CH_3)] was obtained from the reaction of Rh-Cl_3 and H_2TPP in DEF or by warming [TPPRhCl] in the same solvent at 150 °C.

In an attempt to isolate possible intermediate complexes and in order to elucidate the mechanism of formation of such an ethylrhodium derivative, the reaction between rhodium trichloride and porphyrin in DEF was carried out at a lower temperature. Unfortunately no reaction occurs under 150 °C. However, by warming [TPPRhCl] in diethylformamide at 80 °C, under nitrogen for 8 h, we have isolated the complex [TPPRh($NH_2CH_2CH_3$)Cl]. Gas chromatographic analysis of the reaction gases showed the presence of ethylene. If, at the end of this reaction, the temperature was raised to 150 °C the monoethylamino derivative was quantitatively converted to [TPPRhEt].

Pure [TPPRh($NH_2CH_2CH_3$)Cl] appeared to be stable when heated at 150 °C in high-boiling solvents other than DEF.

The expected product (diethylamino)rhodium-tetraphenylporphyrinato, obtained by photochemical addition of diethylamine to [TPPRhCl], is a stable compound. Hence the sequence of reactions observed in diethylformamide cannot be due to the instability of the diethylamino derivative.

A multiple step mechanism may be hypothesized according to the following scheme.



The first ethyl group would be eliminated as ethylene and the second would migrate from the nitrogen atom to the coordinated rhodium, probably through a four-center intermediate.

The reaction solvent (DEF) seems to be very important for the second and third steps of the reaction to occur and this can be attributed to the basicity of the amide. All complexes have been

TABLE 1. ^{1}H NMR data for axial ligands in {[TPPRhL]X} complexes

L	X	H/H^0 (ppm)
CH_3CH_2CO		−1.65 (t, 3H, J = 7 Hz) −3.09 (q, 2H, J = 7 Hz)
CH_3NH_2	Cl	−3.17 (t, 3H, J = 6 Hz) −5.50 (m, 2H)
$CH_3CH_2NH_2$	Cl	−1.64 (t, 3H, J = 7 Hz) −3.40 (m, 2H) −5.63 (m, 2H)
$(CH_3CH_2)_2NH$	Cl	−1.89 (t, 6H, J = 6 Hz) −3.12 (m, 4H) −5.90 (m, 1H)

characterized through IR and NMR spectra and gave satisfactory elemental analysis. Spectral properties of newly synthesized products are reported in Table 1.

^{1}H NMR spectra show the typical strong upfield shift of the resonances of the axial ligands due to the porphyrin ring current [14]. The ligand shielding is responsible for the inversion of the chemical shifts of the methylenic and methyl protons of ethyl- and diethylamino and propionyl derivatives.

Differences in chemical shifts of protons of axial ligands in the newly synthesized complexes with respect to the analogous hexacoordinated species [10], can be attributed to a slight out-of-plane displacement of the rhodium atom, hence to a larger distance from the porphyrin plane in the case of pentacoordinated complexes (see Table 1).

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