

Novel Rhodium Porphyrin Derivatives.

II. Synthesis and Characterization of Hexacoordinated Rh(III) Porphyrinates

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(Received July 29, 1986)

Abstract

Rhodium derivatives of *meso*-tetraphenyl-, octaethyl- and etioporphyrin(I) react with ligands L (L = DMA, *t*-buNC, PPh₂Me, POME₃) thermally or photochemically leading to the corresponding hexacoordinated complexes. The influence of the counter ion on the reaction pathway is discussed.

Introduction

Rhodium macrocycle species have been extensively studied because of the key role of rhodium complexes in catalysis and the possible applications of these compounds as models for biological systems. Numerous papers have appeared in the literature that report on the synthesis of rhodium porphyrin derivatives [1–10]. Although metallation of the macrocyclic ligand can be achieved following standard procedures (*i.e.* the metal carbonyl [11–13] or Adler's DMF method [14]) slight modification of the synthesis conditions may lead to a number of different complexes. Thus several Rh(I) and Rh(III) porphyrins have been prepared using [Rh(CO)₂Cl]₂ as starting material [15–17].

The catalytic role of metalloporphyrin derivatives is certainly dependent on the coordination chemistry of axial ligands [18] but very little has been published up to date on the chemistry of hexacoordinated Rh(III) porphyrins. In a recent paper Kadish [19] has studied the electrochemistry of mono- and bis-dimethylamino derivatives of *meso*-tetraphenylporphyrin, while other research groups have reported on the synthesis of organorhodium derivatives [20–25] and on the reactivity of rhodium porphyrin complexes towards small molecules such as dioxygen and nitric oxide [26, 27].

In a previous paper [28] we reported the synthesis of some hexacoordinated rhodium porphyrins and their spectroscopic characterization. We have now examined the thermal and photochemical reactivity of such species towards ligand addition and substitution reactions.

Results and Discussion

Chloro[octaethylporphyrinatorhodium(III)] can be considered a suitable starting product to synthesize axial substituted derivatives of octaethylporphyrin (H₂OEP). It is known [15] that [Rh(CO)₂Cl]₂ reacts with H₂OEP in benzene leading to μ -octaethylporphyrinato-bis[dicarbonylrhodium(I)] and chloro[octaethylporphyrinatorhodium(III)]. The latter is obtained only in a 20% yield. On the other hand it has been reported [29] that μ -tetraphenylporphyrinato-bis[dicarbonylrhodium(I)] undergoes photochemical oxidation, in the presence of carbon tetrachloride, leading to chloro[tetraphenylporphyrinatorhodium(III)].

The combination of the above cited procedures allowed us to improve the yield of RhOEP-Cl up to 50%. Surprising results have been obtained using toluene instead of benzene as solvent. The product of the reaction is a Rh(III) benzyl derivative previously reported by Ogoshi *et al.* [15]. Other reports on metallation of arenes by rhodium porphyrins dealt with direct electrophilic aromatic substitution reactions [30], whilst alkyl aromatic Rh(III) derivatives have been synthesized [17, 23] by addition of the organic radical deriving from an alkyl halide to (RhOEP)₂ according to a mechanism which has already been established for Co(II) complexes [31, 32]. The strong influence of the solvent on the metallation reaction has also been pointed out when the starting material is RhCl₃. The metal chloride does not react with the ligand in non-polar solvents but, using DMF, aminoderivatives of tetraphenyl and octaethylporphyrin rhodium complexes have been obtained [19, 28].

Hexafluorophosphate rhodium(III) etio-type porphyrinates, such as octaethyl- (OEP) and etioporphyrin(I) (EP), and *meso*-tetraphenylporphyrinates (TPP) easily react with ligands L (L = *t*-buNC, PPh₂Me, P(OMe)₃, DMA) leading to the corresponding RhPL₂PF₆ complexes which have been characterized through analytical and spectral data reported in Tables I and II.

Electronic spectra do not show any remarkable feature: the Rh(III) d⁶ shell seems to be rather inert

TABLE I. Analytical Data for RhPL_nPF₆ Complexes

P	L	n	%C		%H		%N	
			calc.	found	calc.	found	calc.	found
OEP	t-buNC	2	58.20	56.95	6.60	6.55	8.85	8.80
OEP	PPh ₂ Me	2	63.05	62.95	5.95	6.05	4.75	4.75
OEP	P(OMe) ₃	2	47.95	47.50	6.10	5.85	5.30	5.15
OEP	DMA	2	55.15	54.70	6.70	6.45	9.65	8.95
EP	t-buNC	2	56.65	56.60	6.10	5.90	9.45	9.35
EP	PPh ₂ Me	2	61.90	61.90	5.55	5.65	4.95	4.80
EP	P(OMe) ₃	2	46.90	45.90	5.60	5.40	5.75	5.50
EP	DMA	1	53.05	52.85	5.65	5.25	9.10	9.25
TPP	t-buNC	2	63.15	62.30	4.70	4.30	8.20	8.25
TPP	PPh ₂ Me	2	66.65	65.60	3.30	3.80	4.45	4.45
TPP	P(OMe) ₃	2	57.60	56.70	3.90	3.75	5.70	5.75

TABLE II. Spectral Properties of RHPL_nPF₆ Complexes

P	L	n	IR (cm ⁻¹) ^a	¹ H NMR ^b
			ν(NC)	Ligand protons
OEP	t-buNC	2	2221	-0.761s
OEP	PPh ₂ Me	2		-3.095t J(PH) = 3 Hz (CH ₃)
OEP	P(OMe) ₃	2		0.420t J(PH) = 5 Hz
OEP	DMA	2		-3.85d (CH ₃) J = 6 Hz
EP	t-buNC	2	2185	-0.760s
EP	PPh ₂ Me	2		-3.100t J(PH) = 3 Hz (CH ₃)
EP	P(OMe) ₃	2		0.477t J(PH) = 5 Hz
EP	DMA	1		-3.750d J = 6 Hz
TPP	t-buNC	2	2223	-0.650s
TPP	PPh ₂ Me	2		-2.850t J(PH) = 3 Hz
TPP	P(OMe) ₃	2		0.850t J(PH) = 5 Hz

^a Nujol mulls. ^b ppm from TMS; CDCl₃ solutions; s = singlet, t = triplet.

to effects by axial coordination and shows the typical hypso character [33]. The stretching absorption frequencies of the coordinated isocyanides fall in the range 2223–2185 cm⁻¹, quite close to the absorption of the pure species.

In an analogous ruthenium compound the ν(NC) value is lowered to 2106 cm⁻¹ [34]. The higher oxidation state and the positive charge on the central metal atom in the rhodium complexes reduces the back-bonding component from the metal to the axial ligands, quite important in the case of ruthenium. This fact could explain the preliminary evidence that we have obtained [35] on the ease of nucleophilic attacks on the rhodium coordinated isocyanides, whilst such reactions were unsuccessful on ruthenium derivatives.

The ¹H NMR data show, as far as the ligand resonances are concerned, a strong upfield shift which can be explained in terms of anisotropic effect due to the macrocycle ring current [36, 37].

The same octaethylporphyrin derivatives can be obtained by photochemical substitution of dimethylamine from RhOEP(DMA)₂PF₆. These reactions represent one of the few examples of axial ligand photoejection reported for metalloporphyrin derivatives [38].

The starting complex can be obtained either by the reaction of the porphyrin with hydrated rhodium trichloride in DMF followed by anion exchange with AgPF₆ [28] or by reacting RhOEP(Cl) with DMA in the presence of PF₆⁻. Coordination of dimethylamine cannot be thermally achieved when the counter ion of the metalloporphyrin moiety is the chloride ion since the strength of the Rh–Cl bond produces a high barrier for this reaction.

This confirms the results that we previously obtained through 2D NMR experiments with respect to the different interaction that the counter ion may have with the central metal atom [28]. If higher energy is available to the system (irradiation) or a more strongly coordinating ligand, such as a

phosphine, is used, the addition reaction occurs and $\text{RhOEP(L)}_2\text{Cl}$ complexes can be obtained in high yield. The counter ion seems to have a lower effect if the ligand is etioporphyrin(I).

No bis-dimethylamino derivatives have been obtained with this macrocycle. The only literature report on $\text{RhEP(DMA)}_2\text{Cl}$ stated that the synthetic procedure leading to this compound was unreproducible [28, 39].

All the thermal and photochemical reactions we performed on RhEPX and DMA lead always to RhEP(DMA)X no matter if X is Cl^- or PF_6^- . It seems that steric hindrance factors can be excluded because of the capability of the RhEP moiety to coordinate such a large ligand as PPh_2Me , we then suppose that electronic effects are responsible for the addition of only one dimethylamine molecule.

Further studies on the reactivity of the synthesized complexes are currently under investigation.

Experimental

IR spectra were recorded on a Perkin-Elmer Mod. 983 spectrophotometer as nujol mulls. NMR spectra were recorded on a Bruker WP 80SY 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 , H_2OEP and H_2EP were synthesized according to literature procedures [40]. RhTPPCl was prepared following Fleisher's method [3].

Synthesis of RhPCL ($P = \text{OEP}, \text{EP}$)

H_2P (500 mg) and $[\text{Rh}(\text{CO})_2\text{Cl}]_2$ (500 mg) were refluxed, while irradiated with a 200 W halogen lamp, in a benzene-carbon tetrachloride 3:1 mixture for 8 h. The solution was vacuum evaporated and the residue chromatographed on silica gel eluting with benzene-acetone 3:1. Recrystallization from chloroform-methanol afforded the required products. Yields were obtained in the range 30–50%.

Synthesis of RhPL_2PF_6 Complexes

Thermal reactions

RhPCL ($P = \text{TPP}, \text{OEP}, \text{EP}$) (0.5 mmol) and AgPF_6 (1 mmol) were suspended in acetone (30 ml) and stirred at RT, under nitrogen, for about 30 min. The ligand L ($\text{L} = \text{t-buNC}, \text{PPh}_2\text{Me}, \text{POMe}_3$) (2 mmol) was then added. The reaction was monitored by TLC (eluent: chloroform). After 2 h the mixture was evaporated to dryness and the residue recrystallized twice from chloroform-diethylether. Yields were in the range 60–70%.

$\text{RhOEP(DMA)}_2\text{PF}_6$ and RhEP(DMA)PF_6 can be obtained with the above described procedure.

Photochemical reactions

Ligand exchange reactions. $\text{RhOEP(DMA)}_2\text{X}$ ($\text{X} = \text{Cl}^-, \text{PF}_6^-$) (0.5 mmol) and the appropriate ligand (2 mmol) were dissolved in 1,2-dichloroethane (50 ml) and irradiated with a 200 W halogen lamp for 2 h. The volume was then reduced to 10–15 ml and diethylether (50 ml) was added. Products precipitated as large red–purple crystals. Yields were in the range 80–90%.

Ligand addition reactions. $\text{RhOEP(DMA)}_2\text{Cl}$ was obtained by irradiating for 2 h a toluene solution (50 ml) of RhOEPCL (0.5 mmol) in the presence of excess dimethylamine. The product, obtained by vacuum evaporation of the reaction mixture, was chromatographed on silica gel (eluent: chloroform) and recrystallized from chloroform–n-hexane. Yield: 60%.

RhEP(DMA)Cl was obtained by irradiation of a solution of RhEPCL and DMA in 1,2-dichloroethane and purified by column chromatography on Silica gel (eluent: chloroform) and recrystallization from chloroform–diethylether. Yield: 65%.

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