Inorganica Chimica Acta, 119 (1986) 191–194

Novel Rhodium Porphyrin Derivatives

T. BOSCHI, S. LICOCCIA and P. TAGLIATESTA

Dipartimento di Scienze e Tecnologie Chimiche, II Università di Roma, 00173 Rome, Italy

(Received March 25, 1986)

Abstract

Hydrated rhodium trichloride reacts with porphyrins in dimethylformamide to give bis-dimethylamino (DMA) derivatives of general formula [RhP(DMA)$_2$X]. Modifications of the spectral properties caused by anion exchange are discussed.

Introduction

Rhodium porphyrin derivatives have been extensively studied because of the versatile redox behaviour of the central metal ion and their relation to the naturally occurring porphyrin systems [1–4]. As an extention of our studies [5] on the influence of monodentate axial ligands on the redox behaviour and reactivity of ruthenium porphyrins, we decided to investigate rhodium derivatives of octaethyl-(H$_2$OEP) and *meso*-tetraphenylporphyrin (H$_2$TPP). Syntheses of the complexes have been achieved either by reaction of the macrocyclic ligands with [Rh(CO)$_2$Cl]$_2$ in non-coordinating solvents [6–8] or following Adler's method, *i.e.*, reacting the porphyrins with the metal chloride in dimethylformamide (DMF) [9–12].

In a previous paper [13] Gouterman reported that the reaction between RhCl$_3$ and etioporphyrin in DMF lead to decarboxylation of the solvent and incorporation of dimethylamine (DMA) in the resulting metal complex. Further attempts to repeat the synthesis were, however, unsuccessful. With a slightly modified procedure (25% methanol in DMF as solvent), Kalyanasundaram [14] reports that the product of the reaction between RhCl$_3$·xH$_2$O and H$_2$OEP is the complex [RhOEP(L)Cl] where L is a solvent molecule. Identity and purity of this compound were checked by monitoring its intense fluorescence and by means of absorption spectra.

We now report different findings and fully characterize the products of the highly reproducible reactions between hydrated rhodium trichloride and H$_2$OEP or H$_2$TPP in pure DMF.

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. All solvents were reagent grade and were used with no further purification. H$_2$OEP and H$_2$TPP were prepared according to literature procedures [15, 16].

Syntheses of [RhP(DMA)$_2$X] Complexes

$X = [Rh(CO)_2Cl_2]^-, Cl^-$

H$_2$P (500 mg) and RhCl$_3$·xH_2O (500 mg) were dissolved in DMF (250 ml) and refluxed under N$_2$ for 48 h. (If the reaction time is prolonged for 4 days and P = OEP the product is [RhOEP(DMA)$_2$Cl]). The solvent was removed under vacuum and the residue chromatographed on silica gel eluting with chloroform until all the unreacted ligand was separated. The complexes were then eluted with CHCl$_3$/CH$_3$OH 95:5. Recrystallization from chloroform/hexane afforded pure products. Yields were always higher than 75%.

$X = PF_6^-$

300 mg of the appropriate chloride complex were suspended in acetone (50 ml) with the stoichiometric amount of AgPF$_6$. The mixture was stirred for 24 h in a nitrogen atmosphere; the solvent was then evaporated and the residue chromatographed on silica gel eluting with THF. Pure products were obtained either by evaporation of the eluted fractions or by recrystallization from THF/Hexane. Yields were about 90%. Elemental analyses are reported in Table I.

Results and Discussion

Hydrated rhodium trichloride reacts with porphyrins in DMF leading to [RhP(DMA)$_2$]$^+$X$^-$ complexes, the nature of the counter ion depending on the macrocyclic ligand and on the reaction condi-

0020-1693/86/$3.50

TABLE I. Elemental Analyses for $[RhOEP(DMA)_2X]$ Complexes

P	X^-	C%		H%		N%		Cl%	
		Calculated	Found	Calculated	Found	Calculated	Found	Calculated	Found
OEP	$Rh(CO)_2Cl_2$	52.80	51.50	6.10	5.90	8.80	8.30	7.40	8.00
OEP	PF_6	55.15	54.70	6.70	6.45	9.65	8.95		
OEP	Cl	62.94	62.15	7.92	8.00	11.01	10.85		
TPP	PF_6	60.64	61.05	4.45	4.30	8.84	8.40		
TPP	Cl	68.53	69.00	5.03	5.25	9.99	9.45		

TABLE II. Spectral Properties of $(RhP(DMA)_2X)$ Complexes

P	X^-	λ_{max} (nm)	IR (cm^{-1})					^1H NMR		
			ν_{NH}	$\nu_{C=O}$	δ_{Rh-CO}	ν_{Rh-C}	ν_{Rh-Cl}	P–CH	DMA–CH_3	DMA–NH
OEP	$[Rh(CO)_2Cl_2]$	398 512 544	3180	2064 1982	618	492	315 283	10.36	−3.85	−5.5
OEP	$[Rh(CO)_2Br_2]$	398 510 544	3176 1980	2060	602	484		10.36	−3.85	−5.5
OEP	PF_6	395 512 544	3278					10.37	−3.85	−5.5
OEP	Cl	390 515 545(sh)	3160					10.01	−3.95	−5.80
TPP	PF_6	416 526 560	3269					9.01	−3.35	−4.8
TPP	Cl	418 528 560	3400(vbr)					8.95	−3.42	

tions. Thus, in the same experimental conditions, H_2OEP reacts to give $[RhOEP(DMA)_2][Rh(CO)_2Cl_2]$ (**A**), while with H_2TPP we have obtained $[RhTPP(DMA)_2Cl]$ (**B**). The analogous derivative $[RhOEP(DMA)_2Cl]$ (**C**) is obtained with H_2OEP for longer reaction times. All these reactions are reproducible in both anhydrous or reagent grade DMF and afford the products in high yields.

Spectral properties are reported in Table II. The IR spectrum of the octaethylporphyrin derivative A has absorption at 3180 cm^{-1} (NH stretching), two strong bands at 2064 and 1982 cm^{-1} assigned to the carbonyl stretching, and two absorptions at 618 and 492 cm^{-1} which have been attributed to the Rh–CO stretching vibrations. The Rh–Cl stretching bands appear at 315 and 283 cm^{-1}. The frequencies of these bands are quite similar to those reported for $[Rh(CO)_2Cl]_2 \cdot bipy$, $[Rh(CO)_2Cl]_2$ and $(H_4OEP)^{2+}[Rh(CO)_2Cl_2]_2^{2-}$ [3, 17–19].

The ^1H NMR spectrum of complex **A** shows three signals at 10.36 (s, 4H), 4.18 (q, 16H) and 1.97 ppm (t, 24H) due to the porphyrin ring protons and two signals at –3.85 (d, 12H) and –5.15 ppm (br, m, 2H) attributed to the coordinated dimethylamine molecules. The upfield shifts of these signals are attributed to the anisotropic effect due to the macrocycle ring current. Identical spectra were recorded at 300 and 355 K, but irradiation of the signal at –5.5 ppm causes the collapse of the doublet at 3.85 ppm thus indicating the coupling of the DMA methyl and NH protons.

The ^{13}C spectrum shows signals at 182 and 179 ppm (C=O), 144.05 ppm (αC-pyr), 139.98 ppm (βC-pyr), 98.51 ppm (*meso*C), 36.48 ppm (DMA CH_3), 20.02 and 18.66 ppm (ethyl substituents); the chemical shifts are in agreement with literature values [20–22].

Complex A undergoes a metathetical reaction with NaBr, under nitrogen in acetone, leading to $[\mathrm{RhOEP(DMA)_2}]\cdot[\mathrm{Rh(CO)_2Br_2}]$ which was characterized by elemental analysis, IR and NMR spectra.

Under similar conditions $\mathrm{AgPF_6}$ reacts with the counter-ion leading to the corresponding $[\mathrm{RhP(DMA)_2PF_6}]$ complexes.

No 'free' NH stretching has been observed in the IR spectrum of complex B and the proton NMR signals due to the dimethylamine ligands appear as a broad multiplet centered at –3.42 ppm.

When the chloride ion is replaced by hexafluorophosphate, the NH stretching appears as a sharp band at 3629 $\mathrm{cm^{-1}}$ and the NMR spectrum shows a doublet at –3.35 ppm ($\mathrm{DMACH_3}$) and a broad singlet at –4.8 ppm (DMA NH). The spectrum does not change in the temperature range between 255 and 355 K, and decoupling experiments gave the same results as those performed on the octaethylporphyrin derivatives.

It is already known [21] that anion exchange performed with $\mathrm{AgClO_4}$ or $\mathrm{AgBF_4}$ on [RhOEPCl] results in the formation of highly electrophilic Rh(III) porphyrin derivatives capable of direct metallation of arenes. The relevant upfield shift of the NH resonance (about 1 ppm) in the $[\mathrm{RhTPP(DMA)_2PF_6}]$ complex can then be ascribed to a different geometry that the DMA ligand assumes in the presence of a counter ion which forms a looser ion pair. Furthermore, ring current effects are known to be larger on cationic porphyrins [24]; this confirms the existence of a higher density of positive charge on the macrocycle in the case of the $\mathrm{PF_6^-}$ derivative compared to the chloride one.

Although the proton NMR spectra of octaethylporphyrin derivatives are very similar, 2D NMR experiments show some differences. The Nuclear Overhauser Effect (NOE) correlated 2D NMR spectrum of $[\mathrm{RhOEP(DMA)_2Cl}]$ (Fig. 1) exhibits cross peaks between the resonances due to the *meso* protons and $\mathrm{CH_3N}$, respectively, thus indicating a dipole–dipole magnetization exchange between the nuclear species. These cross peaks are present in the 2D NMR spectra of all $[\mathrm{RhOEP(DMA)_2X}]$ complexes regardless of the nature of the counter-ion $\mathrm{X^-}$, but their intensity, normalized with respect to the *meso* protons resonance, is different for the three samples. Assuming as an arbitrary unit the cross peaks' integral for the chloride complex, one finds the ratio 1:0.56:0.35 for $\mathrm{X^-}$ going from $\mathrm{Cl^-}$ to $\mathrm{PF_6^-}$ to $[\mathrm{Rh(CO)_2Cl_2}]^-$. This shows that the dipolar interaction decreases in the order indicated above.

Since NOE depends on the distance between the nuclei, we may conclude that, as in the case of TPP derivatives, the ionic pair of $[\mathrm{RhOEP(DMA)_2X}]$ complexes is tighter going from the $[\mathrm{Rh(CO)_2Cl_2}]^-$ to the $\mathrm{Cl^-}$ counter-ion. Further studies on the 2D NMR spectra of such complexes are in progress.

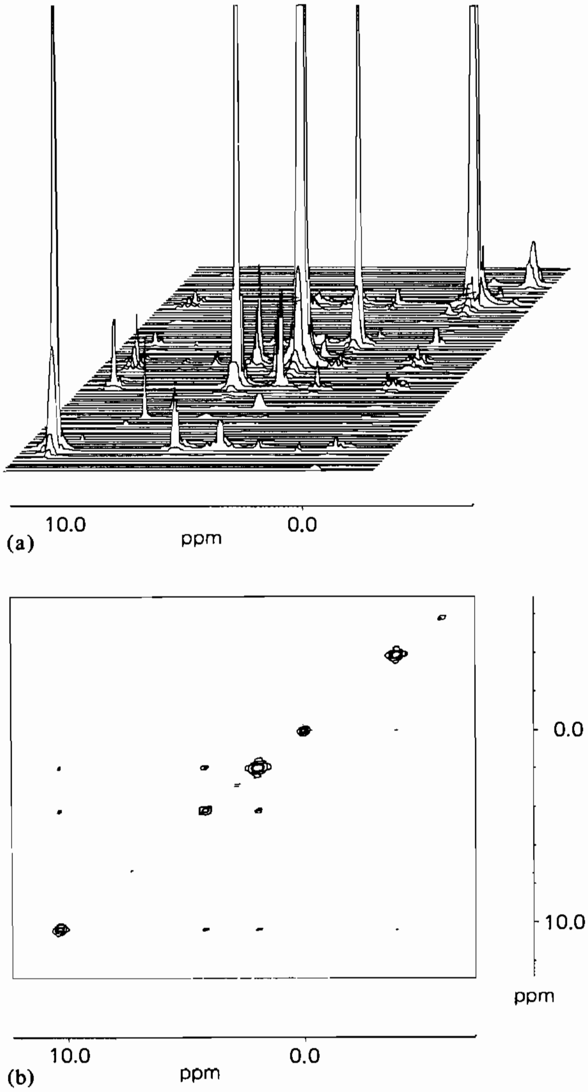

Fig. 1. 2D NOE correlated NMR spectrum of $[\mathrm{RhOEP(DMA)_2Cl}]$ in $\mathrm{CDCl_3}$ (TMS as internal standard): (a) stacked plot; (b) contour plot.

No substitution reactions with phosphine ligands have been observed at room temperature or in refluxing 1,2-dichloroethane.

Thermal and photochemical reactivity of the synthesized compounds are currently under investigation.

Acknowledgements

Many thanks are due to Prof. M. Paci for performing 2D NMR experiments and for many helpful discussions and to Mr. P. Cutraro for his valuable technical assistance.

References

1 D. A. Clarke, D. H. Dolphin, R. Grigg, A. W. Johnson and H. A. Pinnock, *J. Chem. Soc. C,* 881 (1968).

2 B. R. James and D. V. Stynes, *J. Am. Chem. Soc., 94,* 6225 (1972).

3 H. Ogoshi, T. Omura and Z. Yoshida, *J. Am. Chem. Soc., 95,* 1666 (1973).

4 N. Sadasivan and E. B. Fleisher, *J. In. Nucl. Chem., 30,* 591 (1968).

5 T. Boschi, G. Bontempelli and G. A. Mazzochin, *Inorg. Chim. Acta, 37,* 155 (1979).

6 R. Grigg, G. Shelton, A. Sweeney and A. W. Johnson, *J. Chem. Soc., Perkin Trans. 1,* 1789 (1972).

7 A. Takenaka, Y. Sasada, T. Omura, H. Ogoshi and Z. I. Yoshida, *J. Am. Chem. Soc., Chem. Commun.,* 792 (1973).

8 E. B. Fleisher and D. Lavallee, *J. Am. Chem. Soc., 89,* 1132 (1967).

9 J. W. Buchler, in K. W. Smith (ed.), 'Porphyrins and Metalloporphyrins', , Elsevier, New York, 1975.

10 A. D. Adler, F. R. Longo and F. Kampas, *J. In. Nucl. Chem., 32,* 2443 (1970).

11 L. Edwards, D. H. Dolphin, M. Gouterman and A. D. Adler, *J. Mol. Spectrosc., 38,* 16 (1971).

12 M. Gouterman, F. P. Shwartz, P. D. Smith and D. H. Dolphin, *J. Chem. Phys., 59,* 676 (1973).

13 L. K. Hanson, M. Gouterman and J. C. Hanson, *J. Am. Chem. Soc., 95,* 4822 (1973).

14 K. Kalyanasundaram, *Chem. Phys. Lett., 104,* 357 (1984).

15 A. D. Adler, F. R. Longo, J. D. Finarelli, J. Goldmacher, J. Assour and L. Korsakoff, *J. Org. Chem., 32,* 476 (1967).

16 H. H. Inhoffen, J. H. Fuhrhop, H. Voigt and H. Brockman, Jr., *Ann. Chem., 133,* 695 (1966).

17 E. Cetinkaya, A. W. Johnson, M. F. Lappert, G. M. McLaughlin and K. W. Muir, *J. Chem. Soc., Dalton Trans.,* 1236 (1974).

18 L. M. Vallarino, *Inorg. Chem., 4,* 161 (1965).

19 D. N. Lawson and G. Wilkinson, *J. Chem. Soc.,* 1900 (1965).

20 R. J. Abraham, G. E. Hawkes and K. M. Smith, *J. Chem. Soc., Perkin Trans. II,* 627 (1974).

21 L. J. Todd, *J. Organomet. Chem., 77,* 1 (1974).

22 G. M. Bodner and L. J. Todd, *Inorg. Chem., 13,* 1335 (1974).

23 Y. Aoyama, T. Yoshida, K. Sakurai and H. Ogoshi, *J. Chem. Soc., Chem. Commun.,* 473 (1983).

24 R. J. Abraham, *Mol. Phys., 4,* 145 (1961).