

A NEW RHODIUM(I) PORPHYRIN COMPLEX

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Fleischer and Sadasivan^{1,2} have prepared the rhodium(III) porphyrins by the metal incorporation using the reactive rhodium carbonyl chloride $[\text{Rh}(\text{CO})_2\text{Cl}]_2$. Although the Rh(III)-porphyrin complex has been suggested to be produced via Rh(I) porphyrin complex $[\text{porp-Rh}(\text{I})(\text{CO})\text{Cl}]$ based on the spectroscopic study,² no Rh(I) porphyrins have been synthesized so far. We have succeeded in obtaining a new type of Rh(I) porphyrins by the reaction of octaethylporphyrin (OEPH_2) with $[\text{Rh}(\text{CO})_2\text{Cl}]_2$.

A benzene solution of (OEPH_2) and $[\text{Rh}(\text{CO})_2\text{Cl}]_2$ was stirred for 2 hr under the nitrogen atmosphere at room temperature. The dark brown solution was concentrated under reduced pressure. The residual material was chromatographed on silica gel. The first elution with benzene afforded dark green crystals (1) (23% yield), and the second one with acetone-benzene (1:3) gave maroon crystals (2) (44% yield). It is particularly interesting to note that the infrared spectrum of (1) showed four carbonyl stretching vibrations at around 2000 cm^{-1} . The table shows the frequencies of the carbonyl stretching together with those of the carbonyl complexes of octamethylporphyrin(OMPH_2) and tetraphenylporphyrin (TPPH_2), prepared by the similar method.

Table

ligand	$\text{C}\equiv\text{O}$ stretching frequency (cm^{-1})*			
OEP	2045 (s)	2035 (sh)	1983 (s)	1956 (m)
OMP	2051 (s)	2039 (sh)	1999 (s)	1964 (m)
TPP	2080 (sh)	2060 (s)	1985 (s)	1936 (m)

* all spectra were measured in KBr pellets

The i.r. spectra demonstrate the existence of more than two carbonyl groups. The electronic absorption spectrum of (1) in chloroform showed λ_{\max} ($\log \epsilon_{\max}$) at 289(4.37), 367(4.82), 444(4.59), 516(4.14) and 590 $m\mu$ (3.70). Fig. 1 demonstrates the n.m.r. spectra of (1) and (2). The n.m.r. spectrum of (1) in $CDCl_3$ indicated the presence of two magnetically different kinds of $-C_2H_5$ and $-CH=$ groups, which appeared at τ 5.90 (quartet, 8H) and 6.00 (quartet, 8H) for $-\underline{CH}_2CH_3$, 8.11 (triplet, 12H) and 8.33 (triplet, 12H) for $-CH_2\underline{CH}_3$, -0.35 (singlet, 2H) and -0.04 (singlet, 2H) for $-CH=$. The methine proton chemical shifts indicate that the porphyrin ring of (1) has an aromaticity. The mass spectrum showed the most intense peak at m/e 635 assigned to $OEP \cdot Rh(III)^+$. The compound (1) is formulated as an acid, $H^+[OEP \cdot Rh_2(CO)_4Cl]^-$ from the analytical data and the determined molecular weight (890). From the spectral data, (1) is assigned to be the chlorine-bridged Rh(I) complex coordinated with the two adjacent pyrrole nitrogens for each Rh(I) (Figure 2). A medium band at 270 cm^{-1} is probably due to the stretching vibration of the bridging Rh-Cl band.

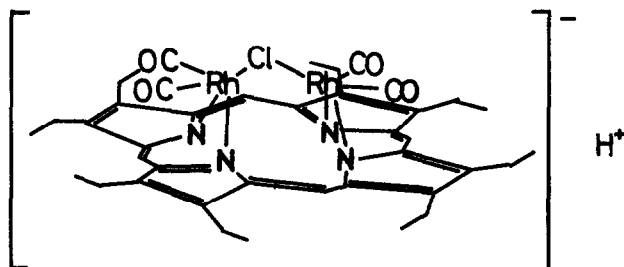


Figure 2 Structure of (1)

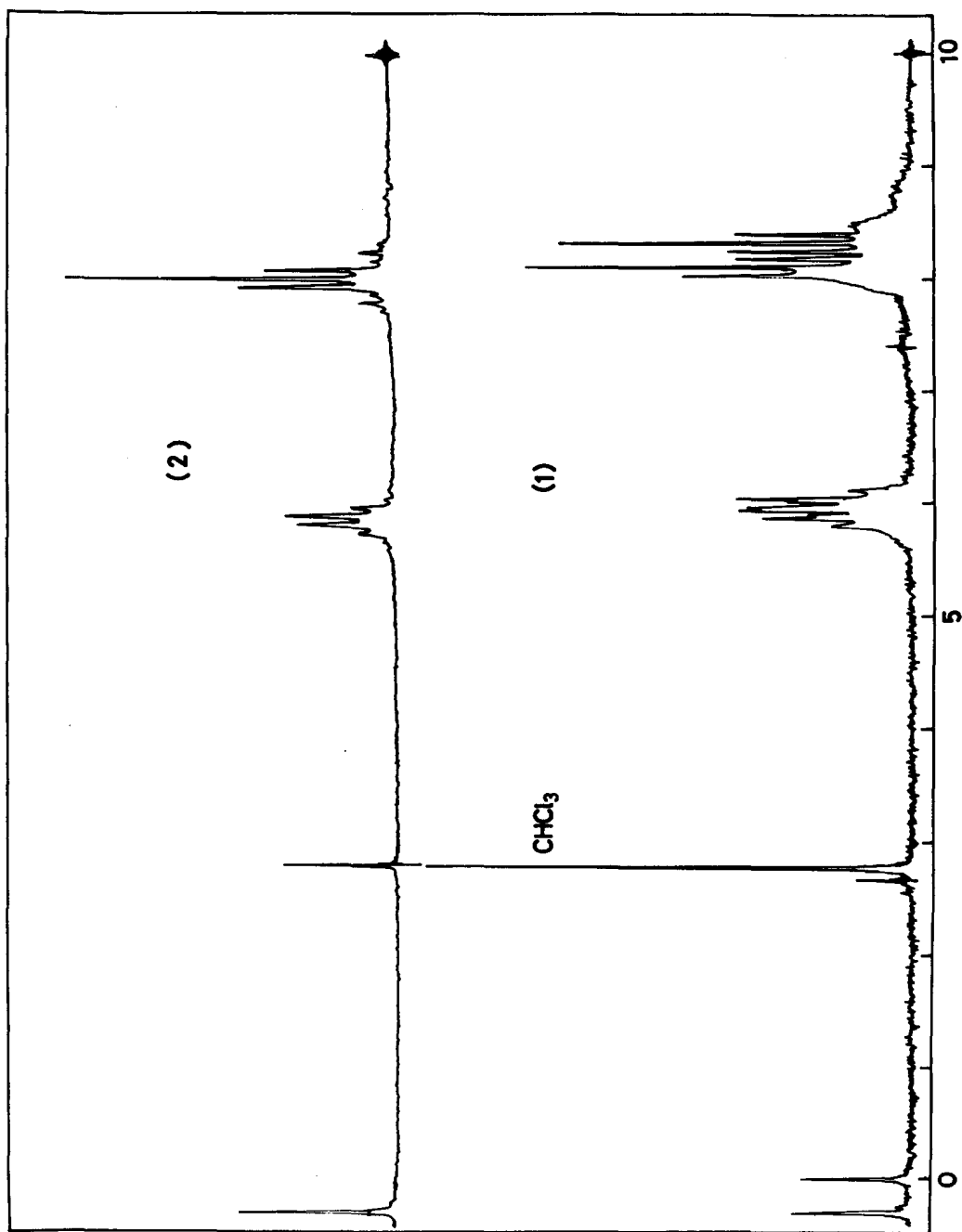


Figure 1 The n.m.r. Spectra of (1) and (2) in CDCl_3 τ (ppm)

The maroon crystal (2) was confirmed to be $\text{OEP}\cdot\text{Rh (III) Cl}\cdot 2\text{H}_2\text{O}$ from the spectral properties together with the elementary analysis. The visible spectrum of (2) in chloroform showed $\lambda_{\text{max}}(\log \epsilon_{\text{max}})$ at 403(5.12), 520(4.12) and 554 $\text{m}\mu$ (4.40). The n.m.r. spectrum gave the proton signals at τ 8.01 (triplet, 24H), 5.85 (quartet, 16H) and -0.31 (singlet, 4H). On exposure to air for several hours the brown spot of (1) on the thin layer chromatogram turned red corresponding to (2). This fact indicates that (2) is formed by the oxidation of (1). The dark brown solution at the initial reaction stage observed by Fleischer and Sadasivan^{1,2} may likely contain the similar chemical species to the isolated compound (1). The reaction of halogeno complex (2) with alkyl lithium afforded the alkyl rhodium complexes. In the n.m.r. spectrum of methyl rhodium complex as one example, the existence of the doublet at τ 16.47 ($J_{\text{Rh-H}}=3.0$ Hz) provides a strong evidence for the formation of $\text{CH}_3\text{-Rh}$ bond. The reaction of (2) with Grignard reagent (RMgX) led to exchange the halogen(X) of RMgX with the chlorine atom of (2).

Reference

- (1) E. B. Fleischer and N. Sadasivan, Chem. Comm. 159 (1967).
- (2) N. Sadasivan and E. B. Fleischer, J. Inorg. Nucl. Chem., **30**, 591 (1968).