Novel Rhodium(I)-Porphyrin Complexes and Organorhodium(III)-Porphyrin Complexes. IV

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Abstract: Two new rhodium(I) porphyrins, porphyrin$[Rh(CO)_2]_2$ (**2**) and *N*-alkylporphyrin$[Rh(CO)_2Cl]_2$ (**4** and **5**), have been isolated during the reaction of $[Rh(CO)_2Cl]_2$ with octaethylporphyrin and *N*-alkyloctaethylporphyrin. Extremely oxygen-sensitive rhodium(I) porphyrin has also been obtained from chlororhodium(III) porphyrin (**3**) by using $NaBH_4$. Organorhodium(III)-porphyrin complexes (**6–19**) have been synthesized by four methods: the reaction of **3** with organolithium compounds, the reaction of Rh(I)-porphyrin complex with alkyl halides, the treatment of the Rh(I) complex with olefins and acetylenes, and the oxidative alkylation of monovalent rhodium *N*-alkylporphyrin.

Cobalt porphyrin with cobalt in its various oxidation states has been considered to be the most plausible model for the coenzyme vitamin B_{12}.[1] However, the cobalt-porphyrin complex has never been utilized as a model for cobalamin due to the inability of the porphyrin ligand to stabilize the Co(I) state in aqueous medium[2] and the low stability of the organocobalt(III) porphyrin, even though the ligand is made of tetrapyrrole.[3] Recently the former problem has been minimized by using the water-soluble porphyrins.[3] The synthesis of a Rh(I)-porphyrin complex formulated as $H[Rh^I(porphyrin)]\cdot 2H_2O$ has been reported by James and Stynes.[4] We have also prepared new Rh(I)-porphyrin complexes during the incorporation of Rh by porphyrin and *N*-alkylporphyrin.[5,6] The alkylrhodium(III) porphyrins were obtainable from the reaction of chlororhodium(III) porphyrin with alkyllithium.[5] The formation of a Rh-C bond in the case of rhodium(III)-$\alpha,\beta,\gamma,\delta$-tetraphenylporphine complexes has been recently reported by two different groups.[7,8] In view of the paucity of information concerned with the reaction of the low valent Rh porphyrin complex in relation to cobalamins, this present report deals with the formation of the Rh(III)-C bond by means of various new synthetic pathways.

Experimental Section

(A) **Rhodium(I) Octaethylporphyrins, 1 and 2.** A mixture of octaethylporphyrin, $OEPH_2$ (744 mg), and $[Rh(CO)_2Cl]_2$ (600 mg) dissolved in 800 ml of benzene was stirred at room temperature for 2 hr. The dark brown solution was condensed into a small portion by evaporation under reduced pressure. The resulting residue was loaded on a silica gel (Wakogel C-200) column. The first elution obtained with benzene yielded upon evaporation dark green crystals **1** (429 mg), which were formulated as $[(OEPH)Rh_2(CO)_4Cl]$.

Anal. Calcd for $C_{40}H_{45}N_4O_4ClRh_2$: C, 54.22; H, 5.01; N, 6.32; Cl, 4.00. Found: C, 54.70; H, 5.11; N, 6.15; Cl, 3.64.

Two recrystallizations from benzene-chloroform gave complex **2**, μ-octaethylporphyrinato-bis[dicarbonylrhodium(I)], which had the following properties: visible spectrum, λ_{max} (log ϵ) in $CHCl_3$, 289 nm (4.37), 367 (4.82), 444 (4.59), 516 (4.14), and 590 (3.70); NMR ($CDCl_3$), τ 8.33 (triplet, $-CH_2CH_3$, 12 H), 8.11 (triplet, $-CH_2CH_3$, 12 H), 6.00 (quartet, $-CH_2CH_3$, 8 H), 5.90 (quartet, $-CH_2CH_3$, 8 H), −0.04 (singlet, $-CH{=}$, 2 H) and −0.35 (singlet, $-CH{=}$, 2 H).

Anal. Calcd for $C_{40}H_{44}N_4O_4Rh_2$: C, 56.79; H, 5.22; N, 6.62; Cl, 0.00. Found: C, 56.48; H, 5.21; N, 6.59; Cl, 0.00.

The second elute with acetone-benzene (1:3) after recrystallization from ethanol yielded 215 mg of maroon crystals **3**, $(OEP)Rh^{III}Cl\cdot 2H_2O$, which had the following properties: mp 300° dec; visible spectrum ($CHCl_3$), λ_{max} (log ϵ) in $CHCl_3$, 285 nm (4.17), 339 (4.26), 403 (5.12), 520 (4.12), and 554 (4.40); NMR ($CDCl_3$), τ 8.01 (triplet, $-CH_2CH_3$, 24 H), 5.85 (quartet, $-CH_2CH_3$, 16 H), and −0.31 (singlet, $-CH{=}$, 4 H).

Anal. Calcd for $C_{36}H_{48}N_4O_2ClRh$: C, 61.17; H, 6.65; N, 7.93; Cl, 5.01. Found: C, 61.36; H, 6.67; N, 7.69; Cl, 5.21.

(B) Reaction of *N*-Alkyloctaethylporphyrin with $[Rh(CO)_2Cl]_2$. A mixture of *N*-ethyloctaethylporphyrin[9] (50 mg) and $[Rh(CO)_2Cl]_2$ (35 mg) dissolved in 50 ml of dry benzene was stirred for 1 hr at room temperature in a nitrogen atmosphere. The end of the reaction was indicated by the disappearance of fluorescence. This solution was evaporated to dryness under vacuum. Recrystallization from chloroform-benzene-pentane yielded 50 mg of violet crystals **4**, which possessed the following properties: mp 96° dec; visible spectrum ($CHCl_3$), λ_{max} (log ϵ), 399 nm (4.69), 427 (4.61), 554 (3.76), 571 (3.84), 596 (3.78), and 616 (3.56). The NMR spectrum of **4** shows eight different methyl signals at τ 8.31, 8.28, 8.24, 8.20, 8.12, 8.10, 8.02, and 7.98 (triplets, $-CH_2CH_3$), four methine protons at −0.30, −0.53, −0.58, and −0.60 (singlets, $-CH{=}$), -NH proton at 13.70 (singlet), NCH_2CH_3 at 16.06 (quartet), and NCH_2CH_3 at 12.57 (triplet). The eight quartets of the $-CH_2$ of peripheral eight ethyl groups are overlapped at around τ 6.0. The ir spectrum of **4** possesses four bands due to the carbonyl stretching modes of terminal carbonyls at 2070, 2050, 2010, and 1957 cm^{-1}, and a band due to the N-H stretching mode at 3170 cm^{-1}. The reaction of *N*-methyloctaethylporphyrin with $[Rh(CO)_2Cl]_2$ gave a similar adduct **5**, which has been described in an earlier study.[6]

(C) **Reaction of 3 with Organolithium (General Procedure).** Freshly prepared alkyl or aryllithium in dry ether was added to a solution of **3** in dry diethyl ether. The reaction procedure was monitored by thin layer chromatography (Merck Kieselgel GF_{254}). The reaction mixture was condensed into a small portion under reduced pressure and extracted with chloroform. The resulting solution was washed with water and dried over anhydrous Na_2SO_4. After evaporation of the solvent, the residue was chromatographed on silica gel using benzene as an eluent. Condensation of the orange elute yielded red crystals. Microanalyses of the prepared organorhodium(III) porphyrins (**6–14**) are summarized in Table I.

n-Butyllithium (1.0 ml of 1.5 *M* *n*-hexane solution) was added to a solution of phenylacetylene (500 mg) in 10 ml of dry ether and stirred for 1 hr. This mixture was added dropwise to the solution of **3** (74 mg) in 50 ml of dry ether. The resulting mixture was vigorously stirred for 30 min, then washed with saturated NH_4Cl aqueous solution and dried over anhydrous Na_2SO_4. Chromatography on silica gel with benzene yielded an orange elute. Crystallization of the condensed residue generates deep red crystals, **15** (30 mg), which can be formulated as $(OEP)Rh^{III}C{\equiv}CC_6H_5$. The ir spectrum of **15** possesses a band at 2115 cm^{-1} due to the $C{\equiv}C$ stretching mode. The proton chemical shifts of the axial phenyl group are observed at τ 5.16 (2 H) and 3.85 (3 H). Anal. Calcd for $C_{44}H_{49}N_4Rh$: C, 71.73; H, 6.70; N, 7.60. Found: C, 70.78; H, 6.62; N, 7.78.

(D) Reaction of Rh(I)-OEP with Alkylhalides (General Procedure). $NaBH_4$ (25 mg, 0.66 mmol) in 3 ml of 0.5 *N* NaOH was added to a solution of **3** (150 mg, 0.220 mmol) in 45 ml of ethanol in argon atmosphere. The resulting mixture was stirred for 3 hr until the color changed from deep pink to brown, indicating the formation of rhodium(I) porphyrin that was rapidly oxydized on exposure to air. A slight excess of CH_3I was added to this mixture.

Table I. Microanalyses, Recrystallization Solvents, and Yield for $(OEP)Rh^{III}R{\cdot}B$

Compound	R	B	Solvent for recrystallization	Yield (%)	Formula	Calcd (%)			Found (%)		
						C	H	N	C	H	N
6	CH_3	None	$ClCH_2CH_2Cl$	46	$C_{37}H_{47}N_4Rh$	68.29	7.57	8.61	68.02	7.22	8.71
7	C_2H_5	None	C_6H_6–petroleum ether	60	$C_{38}H_{49}N_4Rh$	68.66	7.43	8.43	68.91	7.45	8.31
8	n-C_3H_7	None	CH_2Cl_2–n-pentane	54	$C_{39}H_{51}N_4Rh$	69.01	7.87	8.25	68.95	7.65	8.16
9	n-C_4H_9	H_2O	$CHCl_3$–petroleum ether	52	$C_{40}H_{55}N_4ORh$	67.59	7.80	7.88	67.88	7.66	7.89
10	n-C_5H_{11}	None	CH_2Cl_2–n-pentane	36	$C_{41}H_{55}N_4Rh$	69.67	8.12	7.92	68.95	7.97	7.81
11	n-C_6H_{13}	None	CH_2Cl_2–n-pentane	36	$C_{42}H_{57}N_4Rh$	69.98	8.25	7.77	69.86	8.06	7.56
12	n-C_9H_{19}	H_2O	CH_2Cl_2–n-pentane	48	$C_{45}H_{65}N_4ORh$	69.21	8.39	7.17	69.37	8.21	7.29
13	C_6H_5	None	CH_2Cl_2–n-pentane	55	$C_{42}H_{49}N_4Rh$	70.77	7.21	7.86	70.37	7.22	7.66
14	C_7H_7	None	CH_2Cl_2–n-pentane	37	$C_{43}H_{51}N_4Rh$	71.06	7.07	7.71	71.05	6.89	8.02

The reaction mixture was stirred for 10 min, evaporated to dryness, and extracted with benzene. The benzene solution was washed with water and dried over Na_2SO_4. A similar procedure as described in the general method C was applied to isolate $(OEP)Rh^{III}CH_3$ (**6**); the physical properties and spectroscopic values are identical with the original material obtained by method C.

(E) **Reaction of Rh(I)-OEP with Olefins and Acetylenes.** Freshly distilled acrylonitrile (0.5 ml) was added to the solution of Rh(I)-OEP obtained by reduction of **3** (50 mg) under argon atmosphere. The resulting mixture was stirred for 3 hr and then evaporated under vacuum. The residue was extracted with benzene. This benzene solution was washed with water and dried over anhydrous Na_2SO_4. The solvent was evaporated under reduced pressure and the resulting residue was chromatographed on silica column. An orange elute was collected with benzene and then condensed to dryness. Recrystallization from ethanol generated bright red crystals (30 mg) of $(OEP)Rh^{III}CH_2CH_2CN$ (**17**) with the following properties: NMR ($CDCl_3$), τ 15.88 (double triplet, $RhCH_2CH_2CN$), 11.65 (triplet, $RhCH_2CH_2CN$), 8.16 (triplet, $-CH_2CH_3$, 24 H), 6.12 (quartet, $-CH_2CH_3$, 16 H), and 0.26 (singlet, $-CH{=}$, 4 H); visible spectrum (in $CHCl_3$), λ_{max} (log ϵ), 394 nm (5.08), 508 (4.10), and 540 (4.52); ir (KBr), a 2235 cm^{-1} band due to the $C{\equiv}N$ stretching mode.

Anal. Calcd for $C_{39}H_{48}N_5Rh$: C, 67.91; H, 7.01; N, 10.15. Found: C, 68.05; H, 7.06; N, 10.20.

When acetylene gas was introduced into the solution of Rh(I)-OEP, the color of the reaction mixture turned deep pink with immediate formation of red precipitate. The collected precipitate was purified by recrystallization from ethanol-chloroform yielding 77 mg of $(OEP)Rh^{III}CH{=}CH_2$ (**18**). It possessed the following properties: visible spectrum ($CHCl_3$), λ_{max} (log ϵ), 393 nm (5.18), 508 (4.11), and 541 (4.67). The three proton chemical shifts of the axial vinyl group appear at τ 9.40, 11.45, and 12.10 as multiplets.

Anal. Calcd for $C_{38}H_{45}N_4Rh$: C, 68.87; H, 7.15; N, 8.45. Found: C, 68.62; H, 7.19; N, 8.47.

Phenylacetylene (800 mg) was added to a solution of Rh(I)-OEP prepared from 63 mg of **3** under an argon atmosphere at room temperature. This mixture was stirred for 1 hr and evaporated into a smaller portion. A similar purification process as described in general procedure C gave 16 mg of bright red crystals ($(OEP)Rh^{III}CH{=}CHC_6H_5$, **19**). The proton chemical shifts of the styryl group appear at τ 11.88 (double doublets, $J^{103}{}_{Rh-H}$ = 2.5 Hz) and 7.47 (doublet, J_{cis} = 7.5 Hz) due to the cis vicinal protons and at τ 6.27 (doublet, ortho protons, 2 H), 3.51 (triplet, metaprotons, 2 H), and 3.13 (triplet, para proton, 1 H).

Anal. Calcd for $C_{44}H_{51}N_4Rh$: C, 71.35; H, 6.96; N, 7.58. Found: C, 70.43; H, 6.95; N, 7.36.

(F) **Oxidative Alkylation of 4 and 5.** The chloroform solution of **5** was refluxed for 5 hr and then evaporated to dryness. The residue was chromatographed on silica gel. The first elute with benzene was collected and condensed to dryness. Recrystallization from benzene-ethanol yielded the methylrhodium(III) porphyrin, which was confirmed by comparison with complex previously obtained by the reaction of **3** with methyllithium.

(G) **Reaction of 3 with Grignard Reagents.** An excess molar amount of C_2H_5MgI in dry ether (15 ml) was added to a solution of **3** (200 mg) in dry 1,2-dimethoxyethane. The mixture was stirred for 24 hr and then poured into aqueous NH_4Cl solution. The extract obtained with methylene dichloride was washed with water, dried over anhydrous Na_2SO_4, and evaporated to dryness. The solid material was chromatographed on silica gel with chloroform as eluent. The first elute was collected and evaporated to dryness. Recrystallization from a chloroform-petroleum ether mixture generated 150 mg of red crystals (72% yield) formulated as $(OEP)Rh^{III}INH_3$ (**20**). Its properties are as follows: visible spectrum (in $CHCl_3$), λ_{max} (log ϵ), 286 nm (4.10), 333 (4.24), 354 (4.36), 412 (5.01), 525 (4.17), and 556 (4.34).

Anal. Calcd for $C_{36}H_{47}N_5IRh$: C, 55.46; H, 6.08; N, 8.98; I, 16.28. Found: C, 55.50; H, 6.17; N, 8.63; I, 16.56.

The bromorhodium(III) porphyrin, $Rh^{III}(OEP)BrNH_3$ (**21**), was prepared by using C_2H_5MgBr (52% yield). Its properties are as follows: visible spectrum (in $CHCl_3$), λ_{max} (log ϵ), 283 nm (4.05), 330 (4.18), 345 (4.27), 408 (5.05), 524 (4.18), and 554 (4.42).

Anal. Calcd for $C_{36}H_{47}N_5BrRh$: C, 59.01; H, 6.47; N, 9.65; Br, 10.91. Found: C, 58.92; H, 6.87; N, 9.29; Br, 10.89.

Results and Discussion

The existence of monovalent rhodium and iridium complex represented by $[(porphyrin)M^ICOCl]$ has been postulated as a precursor of trivalent metal porphyrin complexes during metal incorporation.[10] Recently we have separated two new Rh(I)-porphyrin complexes, **1** and **2**, with two metal ions bonded to a porphyrin.[5,11,12] Complex **1** liberates HCl in organic solvent. As a matter of fact, two recrystallizations of **1** from CH_2Cl_2 yields the more stable complex **2**. The spectroscopic properties of **2** have been found to be identical with those of **1** in organic solvent. The spectroscopic results reported in the preliminary study should be attributed to complex **2** obtained by liberation of HCl from **1**.[5] The X-ray analysis of **2** shows a structure different from the intermediate complex proposed by Fleischer.[11,12] Two Rh(I) atoms are linked to the porphyrin above and below the porphyrin plane (as is shown in Figure 1). This is however, the first case in which each Rh atom forms square planar coordination with two nitrogens of the four pyrrole rings and two terminal carbonyls. In the case of the Re(I) complex, each Re(I) atom is bonded to the three nitrogen atoms and three carbonyls.[13] The NMR spectrum of **2** is clearly interpretable with a centrosymmetric structure in which $Rh^I(CO)_2$ groups are above and below the plane of porphyrin. In this case, the chemical shifts of the four equivalent methine protons and the eight equivalent ethyl groups in the free base are split into two sets of the $-CH{=}$ and ethyl signals, respectively. Gentle refluxing of a chloroform solution of **2** yielded chlororhodium(III) OEP in moderate yield.

NMR and visible spectra of **4** and **5** indicate low molecular symmetry upon comparison with those obtained for the

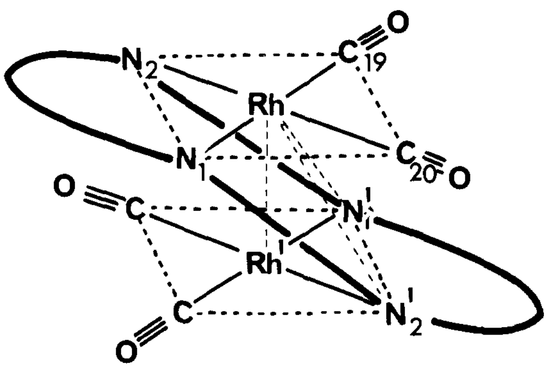


Figure 1. The structure of inner core of $(OEP)Rh^I_2(CO)_4$.[11,12]

free base and the normal metalloporphyrins. However, exact crystallographic studies have not been carried out for the new complexes. Interaction between the Rh(I) atoms and the pyrrolic nitrogen-atom is indicated experimentally by the splitting of the Soret band to 400 and 430 nm. The formation of the complexes **4** and **5** are much faster in comparison with the complex **2**. The rate of metal incorporation by the N-alkylporphyrin is faster by 10^5 than that by the free base.[14] The rate enhancement for the former ligand can be explained by the distortion of the porphyrin ring due to the N-alkylation.[15]

Alkylation of Rh(III) can be performed by treatment of the chlororhodium(III) porphyrin (**3**) with organolithium compounds. The reaction with the Grignard reagent as an alternative pathway resulted in exchange of halogen. Consequently, the bromo- and iodorhodium(III) porphyrin were obtained by the reaction of **3** with RMgBr and RMgI, respectively. On the other hand, the alkyl and aryl cobalt(III) etioporphyrins are obtained by using bromopyridinocobalt-(III) porphyrin and RMgI. Electrophilicity of the Co(III) complex seems to be higher than that of the Rh(III) complex.

$$Rh^{III}ClOEP + RLi \longrightarrow Rh^{III}ROEP + LiCl$$

$$Rh^{III}ClOEP + RMgX \longrightarrow Rh^{III}XOEP + RMgCl$$

Organorhodium(III) porphyrins obtained in this study are much more stable than the organocobalt(III) porphyrin with respect to exposure to the light and moisture. The chemical shifts of methylmetal(III) of $CH_3Rh^{III}OEP$ and $CH_3Co^{III}OEP$ appear at τ 16.5 and 15.2, respectively. Comparison of these values indicates that the Co(III) is more electronegative than Rh(III). Consequently, the Rh(III)-C bond involves relatively higher covalent bonding character.

When the chloro complex **3** is treated with $NaBH_4$ in alcoholic alkaline solution, the visible spectrum of the reaction mixture changes gradually as can be seen in Figure 2. The α-band of the trivalent complex at 550 nm shows a remarkable decrease in absorption strength. The visible spectrum of the reaction mixture is akin to that of $[Rh^ITPP]^-$ obtained by reduction of $Rh^{II}TPP$, in which James and Stynes have isolated the monovalent rhodium complex formulated as $[Rh^ITPP]H$.[4] However, the monovalent rhodium complex could not be isolated in our system. Addition of alkylhalide to our reaction mixture resulted in immediate precipitation. The reaction process was monitored by the visible spectrum as is shown in Figure 2. The cobalt(III) porphyrin complex is not reduced to the Co(I) complex by metal hydride,[1] but can be reduced by a sodium amalgam.[16] Recently, Fleischer and Krishnamurthy have reported that the Co(III) complexes of the water soluble porphyrins are elegantly reduced by $NaBH_4$.[3]

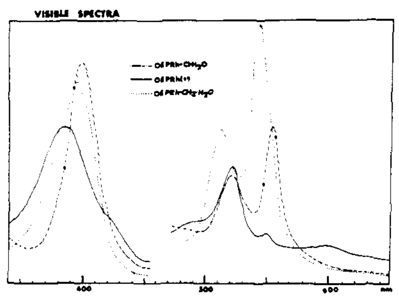
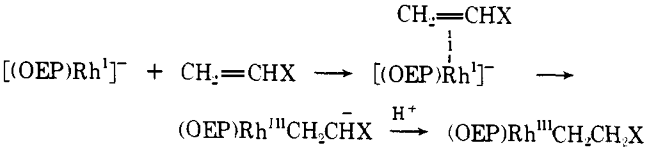


Figure 2. Change in the visible spectrum during the transformation: $(OEP)Rh^{III}Cl{\cdot}H_2O \rightarrow (OEP)Rh^I \rightarrow (OEP)Rh^{III}CH_3{\cdot}H_2O$

The treatment of the solution containing rhodium(I) porphyrin with olefins substituted with the electron-withdrawing group such as acrylonitrile and methyl acrylate gave the alkylrhodium(III) porphyrins in moderate yield. Their NMR spectra show the formation of the Rh-C bond on the β-carbon atom. The scheme of metal-carbon bonding is similar to that of the cobalt(I) glyoxime at a basic pH (pH 9-13).

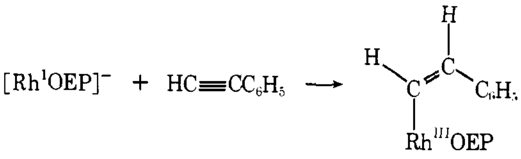
$$[Rh^IOEP]^- \xrightarrow[X = CN, CO_2CH_3]{CH_2=CHX} (OEP)Rh^{III}CH_2CH_2X$$

This reaction may proceed through a π-complex intermediate as has been proposed for addition of olefinic compounds to the cobalt(I) dimethylglyoxime complex.[17] The requirement of electron-withdrawing groups is necessary for stabilization of the negatively charged ion in the σ-complex intermediate.



$$[(OEP)Rh^I]^- + CH_2{=}CHX \longrightarrow [(OEP)\overset{\overset{CH_2=CHX}{\vdots}}{Rh^I}]^- \longrightarrow$$
$$(OEP)Rh^{III}CH_2\overset{-}{C}HX \xrightarrow{H^+} (OEP)Rh^{III}CH_2CH_2X$$

We also noted that the reaction with phenylacetylene yielded only *cis*-styryl($Rh^{III}OEP$) in spite of considerable steric interaction between the phenyl group and the porphyrin ring. Formation of cis-conformer exclusively indicates favorable nucleophilic attack of the Rh(I) to the acetylene in the trans addition mechanism. The cis-conformer **19** has been confirmed by the vicinal coupling constant (J_{cis} = 7.5 Hz). Further support was obtained by a comparison of the NMR spectrum of **19** with that of the trans-conformer **16** prepared from the substitution reaction with trans-bromostyrene (see Figure 3). In the NMR spectrum of **16**, the trans isomer shows a relatively large vicinal coupling constant (J_{trans} = 13.0 Hz). The difference in the chemical shifts of the phenyl groups for both isomers provides an evidence for the stereochemistry of addition reaction. Since the phenyl group of **19** experiences the space subjected to the diamagnetic ring current of the porphyrin ring, these



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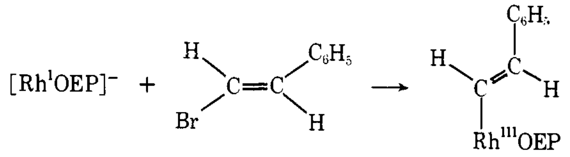

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Table II. NMR Spectra of RRh^{III}OEP in CDCl$_3$ (τ value)

Compound	R	–CH=	–CH_2CH$_3$	–CH$_2$$CH_3$	CHCl$_3$	1^b	2	3	4	5	6	7,8	9
6	–CH$_3$	0.04	5.99	8.10	2.78	16.47							
7	–C$_2$H$_5$	0.03	5.97	8.10	2.78	15.55	14.95						
8	–C$_3$H$_7$	0.02	5.96, 5.98	8.10	2.76	15.61	14.97	12.04					
9	–C$_4$H$_9$	0.04	5.97	8.11	2.76	15.58	15.04	11.93	11.08				
10	–C$_5$H$_{11}$	0.04	5.98	8.11	2.76	15.56	15.02	11.95	10.75	10.44			
11	–C$_6$H$_{13}$	0.03	5.98, 6.00	8.12	(2.77)	15.58	15.04	11.92	10.80	10.11	9.95		
12	–C$_9$H$_{19}$	0.03	6.00, 6.02	8.15	(2.77)	15.68	15.14	11.99	10.83	10.19	9.59	9.15	9.36
						ortho	meta	para	–CH$_3$				
13	–C$_6$H$_5$	–0.09	5.95, 5.99	8.11	2.78	^{a}	5.48	4.96	–				
14	–C$_6$H$_4$CH$_3$-*p*	–0.09	5.95, 6.00	8.11	2.80	7.96	5.64	–	9.07				
15	–C≡CC$_6$H$_5$	–0.15	5.90, 5.92	8.05	2.78	5.16	3.85		–				

^{a} The signal was not detected probably due to the overlapping with the CH$_3$ signals of peripheral ethyl groups. ^{b} Figures indicate the protons of the *n*th carbon atom from rhodium atom.

Table III. The Visible Spectra of the (OEP)Rh^{III}R·B in CHCl$_3$

R	B	λ_{max}, nm (log ϵ) Soret	β	α
CH$_3$	None	396 (5.11)	512 (4.30)	544 (4.51)
C$_2$H$_5$	None	393 (4.92)	509 (3.98)	542 (4.46)
n-C$_3$H$_7$	None	394 (4.95)	510 (3.99)	543 (4.44)
n-C$_4$H$_9$	H$_2$O	396 (5.06)	512 (4.08)	544 (4.52)
n-C$_5$H$_{11}$	None	394 (4.94)	509 (3.99)	543 (4.36)
n-C$_6$H$_{13}$	None	394 (4.77)	510 (3.87)	543 (4.29)
n-C$_9$H$_{19}$	H$_2$O	394 (5.08)	510 (4.13)	543 (4.61)
Ph	None	394 (4.85)	509 (3.96)	542 (4.48)
–C≡CPh	None	401 (5.10)	517 (4.11)	549 (4.44)

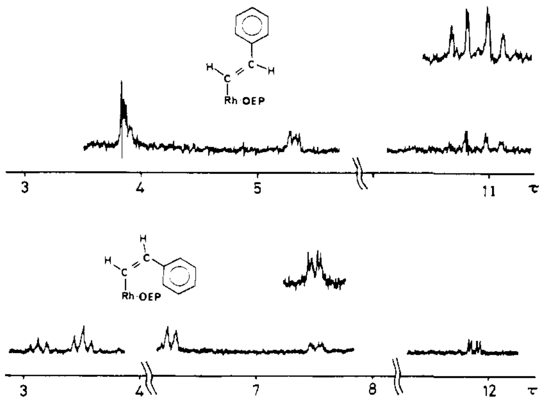


Figure 3. The 100-MHz NMR spectra of the axial styryl groups of cis (19) and trans (16) conformers (τ value in CDCl$_3$).

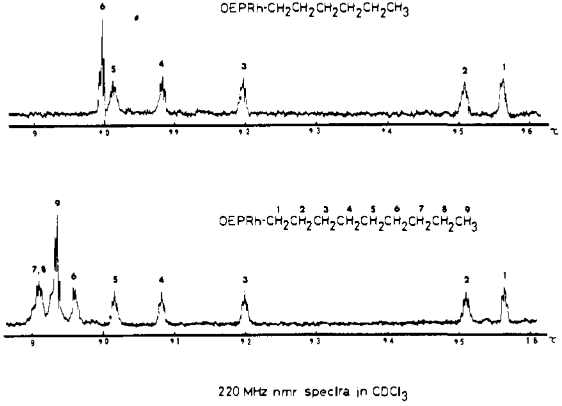


Figure 4. The 220-MHz NMR spectra of axial alkyl groups of *n*-hexyl- (11) and *n*-nonylrhodium(III) OEP (12).

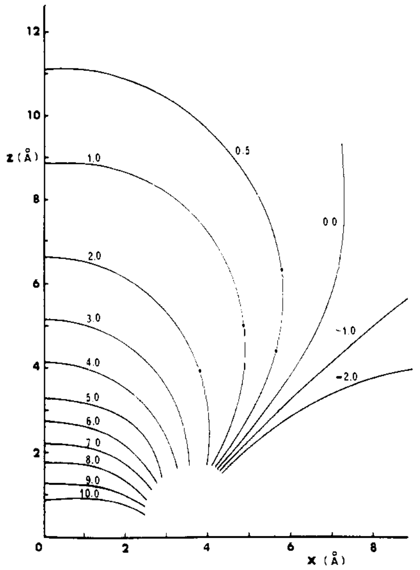


Figure 5. The isoshielding lines of the porphyrin ring in ppm. The *z* axis represents the distance from the ring center along the fourfold axis and the *x* axis represents the distance from the ring center in the ring plane.

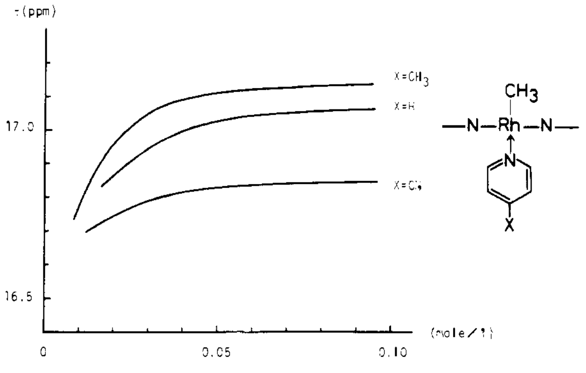
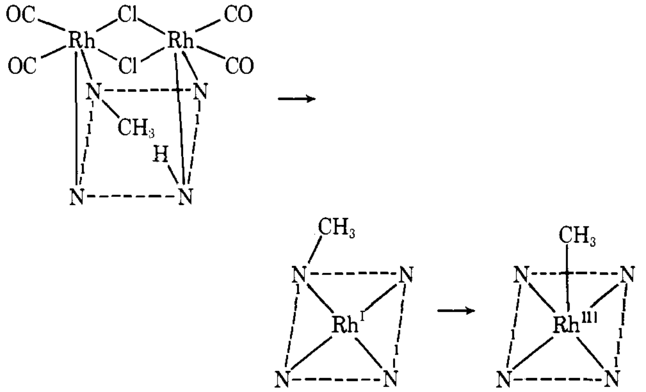


Figure 6. Concentration dependence of the CH$_3$ proton chemical shifts of CH$_3$Rh^{III}OEPC$_5$H$_4$NX (X = CN, H, CH$_3$).

proton chemical shifts appear at higher magnetic fields than those of the trans conformer. It is noted that the reaction of the cobalt(I) glyoxime with phenylacetylene yielded 100% cis isomer.[18-20] The reaction of hydridocobalt(III) glyoxime gave α-styryl(Co^{III}DMG) in contrast to the metal nucleophile.[20] Existence of a hydridorhodium complex is, however, less possible in the present system. The $Rh^{I}OEP$ ion seems to be the preferable complex under basic conditions.

Oxidative Alkylation. The monovalent rhodium complexes **4** and **5** obtained from *N*-alkyl(OEP) and $[Rh(CO)_2Cl]_2$ provide an alternative pathway to form the Rh-C bond. As has been explained in an earlier report,[6] the $N-CH_3$ bond fission is caused by the aid of the low valent rhodium ion. The alkyl migration from the pyrrolic nitrogen to the metal ion may proceed concertedly with oxidation of Rh(I) to Rh(III). Grigg and his coworkers have reported that the divalent metallo-N-alkylporphyrins for Zn(II) and Pd(II) are stable and the N-alkyl bond is not cleaved on complex formation.[21] We have found that reduction of stable $cobalt^{II}NCH_3OEP$ acetate with $NaBH_4$ gave $CH_3Co^{III}OEP$ in good yield.[22] The methyl migration to form a metal-carbon bond leads us to conclude that the oxidative alkylation seems to be initiated by nucleophilic attack of the Co(I) on the methyl group. Methylation of the Rh(I) in the monometal porphyrin proceeds probably in a similar process.



Evaluation of Diamagnetic Ring Current of Organorhodium(III) Porphyrin. The formation of a rhodium-carbon bond by the various methods has been verified by the marked shifts of signals due to the diamagnetic ring current of the porphyrin as is shown in Table II. The chemical shifts of the methyl and methylene directly linked to the Rh(III) atom are split by ^{103}Rh ($I = 1/2$) nucleus and appear at the highest magnetic field. The well-resolved NMR spectra of the axial alkyl groups of *n*-hexyl- and *n*-nonylrhodium(III) porphyrin complexes are shown in Figure 4. These marked shifts can be explained mainly in terms of the diamagnetic anisotropy of the ring current. This approach is reasonable because the chemical shift of the CH_3 of methylaquobis(dimethylglyoximato)rhodium(III) appeared at τ 9.36 (in alkaline D_2O)[23] indicating that the direct effect of the Rh(III) atom on the proton chemical shift through the σ-bond is not large. In order to evaluate the diamagnetic ring current we have made an isoshielding map on the basis of the following assumptions: the Rh-C bond is approximated as 2.0 Å, conformation of alkyl group is linear, and the Rh atom deviates by 0.1 Å from the porphyrin plane. Calculation shifts using the Johnson-Bovey equation[24] deviate from the observed diamagnetic shifts. Seventeen calculated shifts, δ, and observed shifts, $\Delta\tau$, from the corresponding parent hydrocarbons are correlated by the following equation. The value k is taken as 2. The constants a and b were determined as 2.34 and -1.08 by a least-squares method using a computer.

$$\Delta\tau = a(\delta)^{1/k} + b$$

Figure 5 shows a isoshielding map of the organorhodium(III) porphyrin complexes on the basis of the modified Johnson-Bovey equation. The shifts of the protons in close proximity to the central metal atom, especially for α-protons, vary from metal to metal. Therefore, the constants a and b should be readjusted for other metalloporphyrins. It has been, however, found that the proton shifts of the axial ligand away from the central metal appear at approximately same magnetic field as observed for other systems.[25]

Axial Ligand Effect on the Rh(III)-C Bond. Methylrhodium(III) porphyrin complexes involving an amine molecule as a sixth ligand can be regarded as an interesting model compound for methyl and cyanocobalamins. Methyl(amino)rhodium(III) octaethylporphyrin (**22–24**) were obtainable by recrystallization of **6** in an excess molar amount of amine in benzene. These complexes should contain the axially coordinated amine molecules on the basis of their ir spectra and microanalyses. However, interpretation of their visible spectra suggests equilibrium between six-coordinate and pentacoordinate complex. When an excess amount of amine is added to the solution the strength of the Soret and β-band increases, whereas that of the α-band decreases with observed isosbestic points. Similar trends have been observed for $ClRh^{III}(TPP)$, $CH_3CORh^{III}(TPP)$,[7] and $Co^{III}(TPP)$,[26] where TPP denotes the mono(tetraphenylporphyrinato) ligand.

$$CH_3Rh^{III}OEP + L \rightleftharpoons CH_3Rh^{III}OEPL$$

$$L = \text{amine}$$

Figure 6 indicates the changes of the CH_3 proton chemical shifts with changes in the concentration of the six-coordinated complex. The CH_3 chemical shifts approach that of the five-coordinated complex **6** with infinite dilution of the amine complex. Those values are approximately constant in excess molar amounts of amine. The CH_3 signals appear at higher magnetic field in the following order $4-CH_3 > 4-H > 4-CN$ which in turn indicates the strength of trans effect of the amine. The trans effect of amine upon the CH_3 group is explainable on the basis of the predominant σ-donor character of the pyridine derivatives.[27]

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Thermodynamic Data for the Binding of Molecular Oxygen to Cobalt(II) Protoporphyrin IX Dimethyl Ester

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Abstract: Obtaining accurate thermodynamic data for the reversible oxygenation of transition metal ion complexes is critical to an eventual understanding of the factors that influence the strength of binding. The various amine complexes of cobalt(II) protoporphyrin IX dimethyl ester provide a system in which some interesting variations can be examined quantitatively. Thermodynamic results reported by Ibers et al. on this system have been the subject of recent controversy. The conclusions drawn from our method of analysis of the reported data were rejected and our methods criticized. In this paper, we defend our method of analysis and report new experimental data for the O_2 adduct of the pyridine complex of cobalt(II) protoporphyrin IX dimethyl ester under elevated oxygen pressures. Our results differ markedly from those previously reported by Ibers et al. and verify the conclusions arrived at in our earlier analysis.

The binding of molecular oxygen to transition metal complexes in nonaqueous media has been the subject of much current research.[1] By measuring the equilibrium constant at various different temperatures, the corresponding thermodynamic quantities for binding of O_2 can be calculated. In many of the systems reported in the literature (see ref 2a, for example), a great deal of the chemical information is manifested in 1-2 kcal mol^{-1} enthalpy differences. In order to compare one set of data to another, when some chemical variation is made, it is thus necessary that each set be properly evaluated using rigorous procedures for analyzing and reporting experimental quantities. Without such an evaluation, any correlations of these data to other observables becomes at most stochastic if not meaningless. In a previous paper,[2b] we outlined a basic approach to this problem by stating definite criteria for acceptability of calculated parameters from experimental observables. This approach combines not only the objective results of a statistical analysis but also incorporates a time-tested and experience-proven empirical (i.e., common sense) evaluation of one's data to ensure that the values obtained are not the result of the computer converging to a false minimum. Both these criteria have been explicitly stipulated[2b] and, moreover, the combination of both the objective and empirical elements are more desirable than either one or the other by itself.

Statement of the Problem

The fact that the extinction coefficients for the oxygenated and unoxygenated complexes differ permits the equilibrium constant for oxygen uptake to be determined spectrophotometrically. The equilibrium in question is given by

$$\text{py}\cdot\text{CoPIXDME} + \text{O}_2(\text{g}) = \text{py}\cdot\text{CoPIXDME}\cdot\text{O}_2 \quad (1)$$

where py is pyridine and CoPIXDME is cobalt(II) protoporphyrin IX dimethyl ester. The equilibrium constant expression for this system can be written as

$$K = C_C/(C_A - C_C)P_{O_2} \quad (2)$$

where C_A is the initial molar concentration of acid, C_C the *equilibrium* molar concentration of complex, and P_{O_2}, the equilibrium *partial* pressure of oxygen above the solution. Since both the quantities C_C and $(C_A - C_C)$ can be expressed as a percentage of the initial acid concentration, the fraction of acid complexed is to a good approximation, independent of the total acid concentration. Hence, changes in the concentration of acid due to solvent contraction and variations in the molar absorption coefficients over the temperature range studied are of no consequence. This feature is inherent in any 1:1 equilibrium where the concentration of the varied reagent is measured at equilibrium and not determined knowing initial conditions.

An equilibrium constant expression for a 1:1 adduct in terms of measured absorbances has been previously reported[3] as

$$K^{-1} = \frac{A - A^0}{\epsilon_C - \epsilon_A} - C_A - C_B + \frac{C_B C_A}{A - A^0}(\epsilon_C - \epsilon_A) \quad (3)$$

where C_B = initial base concentration in molarity, ϵ_A = molar absorptivity of the acid, ϵ_C = molar absorptivity of the complex, A^0 = absorbance at a given wavelength due to the initial concentration, i.e., $C_B = 0$, and A = absorbance of system at a given wavelength. The only assumption in the derivation of eq 3 is that there are at most two absorbing species (the acid and the complex) which obey Beer's law in the concentration range employed. This equation is readily converted to eq 4 for measurements on the system described in eq 1

$$K^{-1} = P_{O_2}\left[\frac{C_A b(\epsilon_C - \epsilon_A)}{A - A^0} - 1\right] \quad (4)$$

where K is the equilibrium constant associated with eq 1, P_{O_2} is the partial pressure of oxygen above solution, C_A is the initial concentration of acid (total porphyrin concentration) in moles per liter, b is the path length of the absorption cell, A is the total absorbance which is related to the concentration of the oxygen adduct and to the free acid concentration, A^0 is the absorbance of the solution before ad-