Synthesis and Properties of Organocobalt(III)octaethylporphyrins

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The syntheses of alkylcobalt(III)octaethylporphyrins(OEP) *via* nucleophilic attack of the Co(I) complex to unsaturated compounds are reported. Olefins with an electron-withdrawing group and acetylenes react with Co(I)(OEP), whereas olefins with an electron-donating group such as propylene and cyclohexene are unreactive. A novel ring cleavage of cyclopropyl methy ketone initiated by Co(I)(OEP) affords alkylCo(III)(OEP). The reduction of cobalt(II) *N*-methyloctaethylporphyrin acetate results in intramolecular methyl migration from nitrogen to the central cobalt atom. Five-coordination has been established for the organocobalt(III)(OEP) complexes on the basis of their analytical, infrared and NMR data. Some anomalous behavior of the proton signals of the α-carbon atom in their NMR spectra has been discussed in terms of quadrupolar relaxation and electronegativity of the cobalt ion.

The potential nucleophilicity of the d^8 metal ion in a macrocyclic square planar ligand is of particular interest because of its chemical relevance to vitamin B_{12s}[1] and homogeneous catalysts.[2] For example, cobalt(I)[1a,c,f,g] and rhodium(I)[3] ions, bound to a wide variety of square planar ligands, undergo nucleophilic substitution with alkyl halides and addition to olefins and acetylenes, to generate trivalent metal complexes, accompanied by the formation of metal–carbon bonds.

In earlier studies[4] on the rhodium(I)octaethylporphyrin[Rh(I)(OEP)] as a model system of vitamin B_{12}, we have noted novel carbon–carbon cleavage reactions of a number of substituted cyclopropanes and strained polycyclics such as quadricyclene, bicyclobutane, and their derivatives, yielding stable organorhodium(III) complexes. Clarke and his co-workers[5] first reported the synthesis of alkylcobalt(III)etioporphyrin-II by the reaction of Co(I)porphyrin with alkyl halides. The reaction with unsaturated compounds, however, has not been reported previously. We have now examined the generality of these reactions for cobalt(I)octaethylporphyrin. The present work describes the addition to olefins and acetylenes, the ring cleavages of three membered ring compounds, and ring cleavage reaction of cyclopropyl methyl ketone. The novel methyl migration in cobalt(II) *N*-methyloctaethylporphyrin is also reported.[6]

Results and Discussion

Nucleophilic Substitution. A variety of methods to generate cobalt(I) complex as precursor for higher valent cobalt complexes with unsaturated equatorial ligand have been exploited.[1f,g] In this study, the reduction of Co(II)porphyrin was performed by the method used for the generation of Co(I)tetraphenylporphyrin[Co(I)(TPP)][7] and Co(I)etioporphyrin-II [Co(I)(etio)].[5] The NMR spectrum of pyridine-d_5 solution of Co(I)(OEP) thus obtained showed signals at τ 1.03 (s, =CH–), 6.90 (q, $-CH_2-$), and 8.40 (t, $-CH_3$). The chemical shifts are shifted to higher field than those observed for the Co(III)(OEP) complexes, apparently indicating the existence of the low-spin diamagnetic cobalt(I) complex. Attempts to reduce bromopyridinecobalt(III)octaethylporphyrin with sodium borohydride in ethanol to Co(I)(OEP) failed, and only resulted in quantitative formation of Co(II)(OEP). Reduction of Co(II)(OEP) with borohydride in THF was also unsuccessful.

The reaction of Co(I)(OEP) with alkyl halides gave alkyl Co(III)(OEP) in moderate yields. Treatment of Co(I)(OEP) with methyl iodide, ethyl iodide, ethyl 2-bromopropionate, and 2-bromoethylamine yielded the corresponding organocobalt(III)porphyrins (**1**, **2**, **3**, and **4**). The products from benzyl bromide and tertiary alkyl halides were not isolable because of their thermal instability and/or susceptibility to light. Clarks and co-workers[5] have previously assigned a hexacoordinate structure for the alkyl Co(III)(ethio) complex. They proposed a water molecule as the sixth ligand based on the single sharp hydroxy stretching band at 3670 cm^{-1}. No IR absorption due to coordinated water, however, was observed for the OEP complexes, **1**—**4**. In the NMR no signal associated with water protons was detected in $CDCl_3$. These facts together with analytical data led us to conclude that all the alkyl-Co(III)(OEP) complexes are pentacoordinate. Diamagnetic character of these complexes is evidently shown by the positions of chemical shifts and sharp signals of the peripheral ethyl and methene protons. In general, a pentacoordinate structure is a most unusual geometry for the trivalent state of cobalt.[8,9] However a few examples of the isolation of stable pentacoordinate complexes are known for the cobalt(III) complexes of bae.*,[10] Furthermore, it has been argued that a strongly electron-donating ligand would be expected to more easily form a pentacoordinate alkylcobalt(III) complexes in the order bae*>salen*>$(dmg)_2$*>[(do)(doH)pn].*,[11]

trans-β-Bromostyrene reacted readily with Co(I)-(OEP), with complete retention of configuration, to yield exclusively the *trans*-styrylcobalt(III)complex, (**5**). Similarly complete retention of configuration has been reported in the reaction of cobaloxime(I) with *trans*-β-bromostyrene.[12]

Reaction with Olefins and Acetylenes. Addition of the olefins substituted with an electron-withdrawing group to a tetrahydrofuran solution of Co(I)(OEP),

* Abbreviations used: bae, *N,N'*-ethylenebis(acetylacetoneiminato); salen, *N,N'*-ethylenebis(salicylideneiminato); dmg, dimethylglyoximato; [(do)(doH)pn], 1,3-bis-(biacetylmonoximeimide)propane.

Table 1. Microanalysis of Co(III)(OEP) complexes

Compound	Formula	C(%) Found	C(%) Calcd	H(%) Found	H(%) Calcd	N(%) Found	N(%) Calcd
(1)	$C_{37}H_{47}N_4Co$	72.76	73.24	7.83	7.80	9.31	9.23
(2)	$C_{38}H_{49}N_4Co$	72.45	73.52	7.74	7.96	8.84	9.03
(3)	$C_{41}H_{53}N_4O_2Co$	71.08	69.62	7.72	7.71	8.04	8.09
(4)	$C_{38}H_{50}N_5Co$	68.77	71.67	7.50	7.86	11.00	11.00
(5)	$C_{44}H_{51}N_4Co$	76.00	76.08	7.43	7.40	8.18	8.06
(6)	$C_{39}H_{48}N_5Co$	72.24	72.50	7.65	7.48	10.81	10.84
(7)	$C_{38}H_{47}N_4Co$	72.81	73.64	7.89	7.80	8.94	9.04
(8) [a] (9) [a]	$C_{44}H_{51}N_4Co$	75.80	76.08	7.34	7.40	8.20	8.06
(14)	$C_{38}H_{49}N_4OCo$	71.75	71.67	7.55	7.76	8.80	8.80
(15)	$C_{41}H_{53}N_4OCo$	72.59	72.76	7.84	7.89	8.67	8.28
(16) [b]	$C_{37}H_{46}N_4ClCo$	68.96	68.98	7.46	7.56	8.69	8.94
(17)	$C_{39}H_{50}N_4O_2Co$	69.90	70.35	7.63	7.53	8.40	8.46

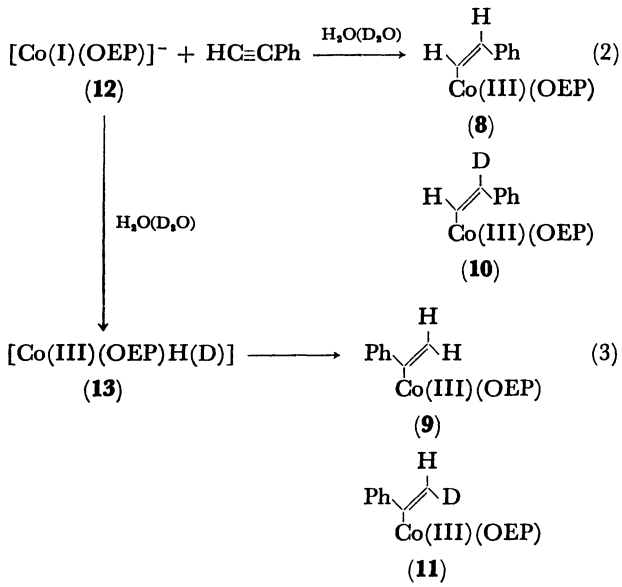
a) A mixture of (8) and (9). b) Analysis of Cl; Calcd: 5.95%. Found: 5.53%.

followed by treatment with a portion of aqueous alkali (0.1 N) gave exclusively β-substituted alkylcobalt(III)-porphyrins, (6) and 3, in moderate yield (Eq. 1). It was clearly proved by the NMR signals due to the

$$[Co(I)(OEP)]^- \xrightarrow[2.\ H_2O\text{-}NaOH]{1.\ CH_2{=}CHX} Co(III)(OEP)\cdot CH_2CH_2X \quad (1)$$

X: CN, (6); CO_2Et, (3)

axially coordinated alkyl protons that the bond formation had taken place at the β carbon atom (*vide infra*). This is also supported by the fact that the product obtained from ethyl acrylate was identical with an authentic sample of 2-(ethoxycarbonyl)ethylcobalt(III)(OEP) (3). In marked contrast to the olefins with an electron-withdrawing substituent, the reaction with propylene and cyclohexene resulted in spontaneous formation of divalent cobalt complex before addition of aqueous alkaline solution. As has been proposed in the reaction of cobaloxime(I) and other Co(I) complexes with olefins,[1f,g] it seems that the reaction species is not a hydrido complex (13) but rather a complex anion (12). However, the presence of 13 cannot be completely excluded under the present conditions since a small amount of the α-styryl complex (9) was formed in the reaction with phenylacetylene as described below.



(2)

(3)

Introduction of acetylene gas into the THF solution

Table 2. Visible spectra and characteristic infrared spectra of cobalt OEP complexes

λ_{max} (nm) (log ε_{max}) in $CHCl_3$

	I	II	III	IR bands (cm^{-1}) [c]	Assignment
$[Co(I)(OEP)]^-$	396 [a]	520 [a]	548 [a]		
(1)	393 (5.34)	519 (4.02)	552 (4.37)		
(2)	392 (5.30)	520 (4.00)	551 (4.37)		
(3)	392 (5.27)	517 (4.02)	551 (4.41)	1750	ν(C=O)
(4)	388 (5.28)	524 (4.01)	554 (4.43)	3250, 3305	ν(N-H)
(5)	393 (5.38)	524 (4.02)	556 (4.44)	1490, 1558, 1585, 3050, 720	Phenyl vibrations
(6)	391 (5.25)	519 (4.02)	552 (4.45)	2225	ν(C≡N)
(7)	392 (5.40)	520 (4.01)	554 (4.45)	1568	ν(C=C)
(8) (9)	394 [b]	525 [b]	556 [b]	1590, 1600, 1610, 3050, 3300, 698	Phenyl vibrations
(14)	392 (5.31)	520 (4.01)	552 (4.43)	3570	ν(O-H)
(15)	392 (5.24)	520 (3.96)	552 (4.43)	1720	ν(C=O)
(16)	392 (5.30)	524 (3.97)	554 (4.36)	695	ν(C-Cl)
(17)	428 (4.80)	542 (3.78)	588 (3.92)	1615	ν(C=O)

a) Measured in THF. b) A 3: 1 mixture of (8) and (9). c) Measured in a KBr disk.

TABLE 3. ^{1}H NMR SPECTRA (100 MHz) OF ORGANOCOBALT(III)OEP COMPLEXES IN $CDCl_3$ (τ value)

	Assignment						
	Equatorial ligand			Axial ligand			
	$=CH_2-$	$-CH_2-$	$-CH_3$	H_a	H_b	H_c	H_d
(**12**)	1.03(s, 4H)[a]	6.90(q, 16H)[a]	8.40(t, 24H)[a]				
(**1**)	−0.08(s, 4H)	6.00(q, 16H)	8.12(t, 24H)	15.20(brs, 3H)[b] 15.30(s, 3H)[b,c]			
(**16**)	−0.39(s, 4H)	5.73(q, 16H)	7.90(t, 24H)	12.03(brs, 2H) 12.53(s, 2H)[c]			
(**2**)	0.00(s, 4H)	6.00(q, 16H)	8.11(t, 24H)	14.08(br) 14.38(q, 2H)[c]	15.47(t, 3H) 15.23(t, 3H)[c]		
(**3**)	−0.01(s, 4H)	5.98(q, 8H) 6.02(q, 8H)	8.13(t, 24H)	12.71—16.72(br) 14.34(m, AA'BB', 4H)[c]	14.22(br)	7.11(q, 2H)	9.64(t, 3H)
(**6**)	−0.07(s, 4H)	5.98 5.99 (dq, 16H)	8.12(t, 24H)	14.28 (br, 4H)			
(**14**)[h]	−0.05(s, 4H)	5.99 6.01 (dq, 16H)	8.14(t, 24H)	14.36(br)	13.08(t, 2H)		
(**4**)[e]	−0.03(s, 4H)	5.86(q, 16H)	8.14(t, 24H)	16.17(br)	12.75(br)		
(**15**)	0.02(s, 4H)	6.02(q, 16H)	8.15(t, 24H)	14.37(br, 2H) 14.70(m, 4H)[c]	15.00(qu, 2H)	10.90(t, 2H) 10.70(t, 2H)[c]	9.38(s, 3H) 9.50(s, 3H)[c]
(**7**)	−0.09(s, 4H)	5.97(q, 8H) 6.00(q, 8H)	8.13(t, 24H)	10.81(brm, 1H) J_{ab}=4.0, J_{bc}=4.0, J_{ac}=13.0 Hz	10.26(t, 1H)	12.00(q, 1H)	
(**8**)[d]	0.17 (s)	6.03(q) 6.05(q)	8.14(t)	9.94(br) J_{ab}=4.0 Hz	11.30(d)	6.10(m)[f]	3.50(m)[g]
(**9**)[d]	−0.05(s)	6.00(dq)	8.14(t)	10.85(d)	12.67(d)	7.73(m)[f]	4.33(m)[g]
(**5**)	−0.11(s, 4H)	5.98(q, 8H) 6.00(q, 8H)	8.12(t, 24H)	10.12(brd, 1H) J_{ab}=12 Hz	11.00(d, 1H)	5.10(m, 2H)[f]	3.79(m, 3H)[g]

Abbreviations used: s, singlet; d, doublet; t, triplet; q, quartet; qu, quintet; m, multiplet; br, broad.
(**1**), $-C(H_a)_3$; (**2**), $-C(H_a)_2C(H_b)_3$; (**3**), $-C(H_a)_2C(H_b)_2CO_2C(H_c)_2C(H_d)_3$; (**4**), $-C(H_a)_2C(H_b)_2NH_2$; (**5**), $-C(H_a)=C(H_b)Ph$; (**6**), $-C(H_a)_2C(H_b)_2CN$; (**7**), $C(H_a)=C\begin{smallmatrix}(H_b)\\(H_c)\end{smallmatrix}$; (**8**), $-C(H_a)=C(H_b)Ph$; (**9**), $CPh=C\begin{smallmatrix}(H_a)\\(H_b)\end{smallmatrix}$; (**14**), $-C(H_a)_2C(H_b)_2OH$; (**15**), $-C(H_a)_2C(H_b)_2COC(H_d)_3$.
a) Measured in pyridine-d_5. b) Measured at 220 MHz. c) Measured in the presence of pyridine. d) A 3: 1 mixture; for details, see Discussion. e) NH: not detected. f) Phenyl, *o*-H. g) Phenyl, *m*-H and *p*-H. h) OH: not detected.

of Co(I)(OEP) gave vinylcobalt(III)(OEP) (**7**) isolated in 19% yield. Phenylacetylene readily reacted with the Co(I)(OEP) and the product (29% yield based on the NMR spectrum) was found to be a mixture of *cis*-β-styryl (**8**) and α-styrylCo(III)(OEP) (**9**). They were not separable by chromatography.

The ratio of isomers **8** and **9** was determined as 3: 1 by intensity ratio of the *meso*-proton chemical shifts at τ 0.17 and −0.05. As demonstrated in Table 3, full assignments of the NMR signals were accomplished by comparing the spectra of complexes **8** and **9**, with that of the *trans*-conformer **5** and that for mixture of partially deuterated styryl complexes (**10**) and (**11**) prepared from deuteration experiments. Assignments were also confirmed with the aid of the spectra for the corresponding *cis*- and *trans*-β-styryl rhodium(III)(OEP) complexes.[4] The relatively small vicinal coupling constant (4.0 Hz) compared to that observed for **5** (J_{trans}=12.0 Hz) rationalizes the stereochemistry of *cis*-conformer **8**. The α-styryl complex **9** has been also confirmed by the β-carbon proton signals at τ 10.85 and 12.76 with the coupling constant of 1.5 Hz due to geminal protons. Furthermore, inspection of molecular models suggests that anisotropic shielding of a phenyl group in the *cis*-conformer **8** causes high field shifts of the *meso*-positions and in turn the phenyl group would experience the ring current of the porphyrin ring. Thus the higher field peak at τ 0.17 is assigned to the *meso*-protons of **8**. The chemical shifts of the phenyl protons appear at a higher magnetic field than those of the *trans*-conformer **5**.

For cobaloxime(I), it has been reported that a mixture of α-styryl and *cis*-β-styryl complexes is formed in a mildly alkaline solution.[12,13] The formation of an α-styryl complex may arise from a hydridocobalt(III) complex (**13**) as has been discussed for the cobaloximes.[12-15] The reaction yields for the acetylenic compounds are considerably lower due to the generation of Co(II)(OEP) during chromatography. In contrast, the reactions of cobaloxime and Rh(OEP) with acetylenic compounds give quantitative formation of the vinylmetal complexes.[4,12-15] It is of interest to note that the Co(I) complex of the water soluble porphyrin catalyzes only the reduction of acetylene[16] whereas we have obtained the vinylcobalt(III) complex **7**. Thus, low yields may be in part ascribed to the homolytic decomposition of the carbon–cobalt(III) bond to Co(II)(OEP) and a radical species.

Reaction with Three Membered Ring Compounds. Co(I)(OEP) reacted readily with ethylene oxide and ethyleneimine to yield 2-hydroxyethyl- and 2-aminoethylcobalt(III)(OEP), **14** and **4**, respectively. The cleavage of the C–X bond was confirmed by the IR and NMR spectra. For example, **14** shows a sharp hydroxy stretching vibration at 3570 cm^{-1} and NMR

$$[Co(I)(OEP)]^- + \triangle^{X} \xrightarrow{H_2O} Co(III)(OEP)\cdot CH_2CH_2XH \quad (4)$$

X: O, (**14**); NH, **4**

signals at τ 14.36 and 13.08, assigned to α-and β-carbon protons of the axially coordinated alkyl group respectively. Likewise reaction of ethyleneimine gave the 2-aminoethyl analogue, identical with the product obtained from β-bromoethyl amine. The analytical values of the product are somewhat poor, presumably due to its low stability in the crystalline state. However, the infrared spectrum shows clear bands at 3250, 3305 cm^{-1}, characteristic of the N–H stretching vibration of the primary amino group.[17] In the NMR spectrum two signals assignable to the α- and β-methylene protons are observed at τ 16.17 and 12.75, respectively. These spectral data support the proposed structure **4**.

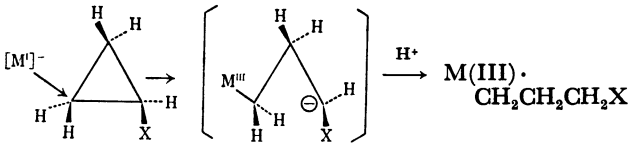
As described in the introduction, Rh(I)(OEP) cleaves cyclopropanes with an electron-withdrawing substituent to form the Rh–C bond at the γ-position with respect to form the Rh–C bond at the γ-position with respect to the substituent.[4] This fact is surprising since the cyclo-

$$[M(I)(OEP)]^- + X\text{-}\overset{2}{\underset{1}{\triangle}}\overset{}{\underset{3}{}} \xrightarrow{H_2O} M(III)(OEP)\cdot {}^{\alpha}CH_2{}^{\beta}CH_2{}^{\gamma}CH_2X \quad (5)$$

M=Rh: X=CH_3CO, CO_2Et
M=Co: X=CH_3CO, (**15**)

propane ring is considered to be stable towards the nucleophilic attack, and in general cleavage of cyclopropane ring by nucleophiles proceeds under severe conditions.[18] At room temperature, treatment of $[Co(I)(OEP)]^-$ with cyclopropyl methyl ketone gave readily 4-oxopentyl-cobalt(III)(OEP) (**15**). The ring fission along the 1, 2 bond was verified by the NMR spectrum which showed a broad signal at τ 14.37, a multiplet at 15.00 and a triplet at 10.90, assignable to α-, β-, and γ-carbon protons, respectively. A sharp singlet due to the terminal methyl group was observed at τ 9.38. However, no product was obtained for cyanocyclopropane but reaction with ethyl cyclopropanecarboxylate gave a small amount of product which showed a sharp carbonyl stretching absorption at 1720 cm^{-1}. In both cases, chloromethylcobalt(III)(OEP) (**16**) was isolated as a major product by the competitive substitution with the solvent methylene chloride. This result indicates that the reaction with cyclopropyl derivatives to form a σ bond is relatively slow and the unreacted Co(I) complex anion still remained in the reaction mixture.

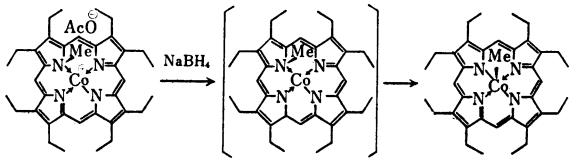
In rhodium octaethylporphyrin the *endo*-configuration has been established for the product obtained from nortricyclanone.[19] It has thus been suggested that cleavage of the cyclopropyl ring by a rhodium(I) anion follows a S_N2 mechanism, *e.g.*, the reaction does not proceed *via* a π-type complex formed between the cyclopropane and the complex anion but rather *via* an intermediate carbanion stabilized by an electron-withdrawing substituent (Scheme 1). The observed activation by an acyl group may imply a similar mechanism.



Scheme 1.

Weber and Schrauzer have reported that rhodoxime(I) is less nucleophilic than cobaloxime(I) in the substitution with alkyl halides.[20] Marked difference in the reactivity between Co(I)(OEP) and Rh(I)(OEP), however, may arise from the difference in stability of the various oxidation states. For metalloporphyrins, the cobalt ion is able to exist in the various oxidation states such as Co(I), Co(II) and Co(III).

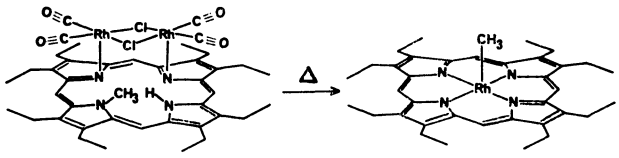
Intramolecular Methyl Migration to Cobalt Atom. Reduction of Co(II) *N*-methyloctaethylporphyrin acetate $[Co(II)(N\text{-}MeOEP)]^+OAc^-$ (**17**) with sodium borohydride proceeded to completion in thirty minutes at room temperature. The expected monovalent complex (**18**) was not obtained, but the trivalent cobalt-methyl derivative **1**, generated in 58% yield.



17 **18** **1**

In contrast with the complicated visible spectra of *N*-alkyl metalloporphyrin,[21] the generated complex showed a characteristic spectrum of metalloporphyrins.[22] Conclusive evidence for the cobalt–methyl bond was provided by the NMR spectrum which is identical with that observed for **1**. The complex is also identical with the protuct obtained by the substitution of pyridinebromocobalt(III)(OEP)[21] with methyl lithium. Grigg and co-workers[23] have reported that alkyl groups in Ni(II) and Pd(II) *N*-alkyl corroles migrate thermally from the pyrrolic nitrogen to the β-carbon atom of the pyrrolic ring. Perhaps the methyl migration proceeds through nucleophilic attack of the Co(I) ion, which may be assisted by the release of strain in the porphyrin ring coordination.

Previously we observed the migration of an alkyl group from nitrogen to the central metal atom for the dirhodium(I) complex of *N*-alkyl OEP (**19**) concomitant with the oxidation of the monovalent state of the metal, yielding alkylmetal(III) σ-complexes.[4] The present study suggests that the alkyl migration in the complex **19** proceeds *via* an intermediate analogous to



19 1

the postulated monovalent metal complex **18**. The present alkyl migration can be considered to be an intramolecular oxidative addition through the C–N bond to the Co(I) ion.

^1H NMR Spectra. Table 3 lists the NMR spectra of the alkylcobalt(III) complexes. Structures are proposed on the basis of the proton chemical shifts of the axially coordinating alkyl groups. These protons experience the influence of the ring current of the porphyrin macrocycle. The chemical shifts for the methyl and ethyl complexes **1** and **2** are quite similar to those observed for the corresponding aquoalkylcobalt(III) complexes of etioporphyrin II.[6] The hydrogens of the carbon directly attached to the cobalt atom (denoted as H_a in Table 3) appear at lower field as compared with those for other corresponding alkyl metalloporphyrins. For example, methyl hydrogens in the complex **1** resonate at τ 15.20, whereas the chemical shifts of the methyl hydrogens in Rh(OEP)·CH_3·H_2O[4] and Ge(porphin)$(CH_3)_2$[24] appear at 16.47 and 17.98, respectively. The hydrogens in the alkyl group for Rh(OEP)·R·H_2O, and Ge(porphin)(R_2) appear in the expected order C_α–H_2>C_β–H_2>C_γ–H_2……. In contrast, the methyl protons in the ethyl complex **2** resonate at lower magnetic field than those of the methylene protons. This lower field shift of the C_α-hydrogen can be explained if we assume that the cobalt(III) ion in the organocobalt porphyrin is more electronegative than those of other metals. This explanation seems to be reasonable since the geminal coupling constant in the vinyl complex **7** is relatively large (J_{gem}=4.0 Hz) as compared with those (<1 Hz) for other vinyl metal complexes.[4,12,13] In general, a large geminal coupling constant is associated with a high electronegativity of the substituent of the vinyl derivatives.[25]

Figure 1 shows representative spectra of Co(III)(OEP)R in the high field region in $CDCl_3$. Anomalous line broadening has been observed for the proton signals of α-carbon atom. The broadening is common to all the complexes. The rest of the signals of the axial alkyl group are all normal, indicating the absence of dimer-formation in solution as reported for cobaloximes.[26] Clarke and his co-workers have ascribed similar line broadenings for the C_α-hydrogens in etioporphyrin II to the poorly resolved nuclear spin-spin coupling between ^{59}Co–^{1}H.[6] If this is true, it seems rather surprising since the naturally occurring cobalt (100%, ^{59}Co) has a large electric quadrupole moment, Q= 0.5×10^{-24} cm^2 [27] and hence spin-spin coupling between protons and a nucleus is normally not observed in solution due to rapid spin-relaxation of the quadrupolar nucleus.[28] Accordingly, spin coupling between protons and cobalt has never been observed for either the pentacoordinate[29] or hexacoordinate alkyl cobalt σ

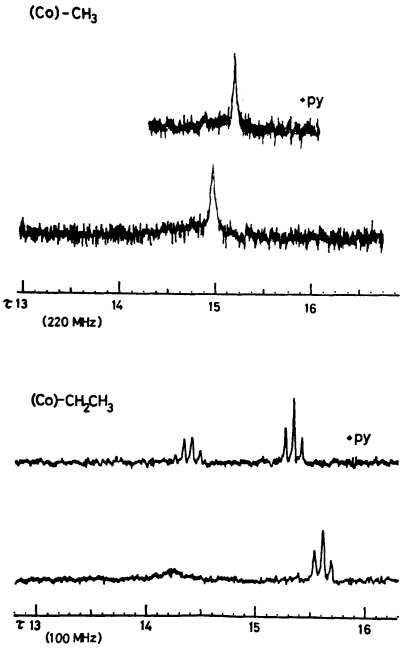


Fig. 1. NMR spectra of **1** and **2** in the high field region (measured in $CDCl_3$).

complexes hitherto reported. As is shown in Fig. 1, the signal shape was appreciably sharpened to give well resolved hyperfine structure when an excess amount of pyridine was added. Consequently, the expected quartet of the methylene group at τ 14.38 could definitely be identified for the ethyl cobalt(III)(OEP) **2**. Concomitantly, signal due to C_α-hydrogens was shifted to higher field by 0.4—0.5 ppm while slight shift to lower field was observed for the signal due to C_β-hydrogens. These observations lead us to postulate that the broadened line shape of the C_α-hydrogens is due to partially relaxed cobalt–proton coupling caused by quadrupolar relaxation. Similar phenomena have been observed for tricarbonyl(η-cycloheptatrienyl)vanadium(I)[30] and the mechanism is well understood.[28] The rate of relaxation depends on the strength of the coupling between the quadrupole moment and fluctuating electric field gradients at quadrupolar nucleus.[28] The electric field gradient at the cobalt atom in the pentacoordinate porphyrin complex might be weak; in consequence, despite a relatively large value of Q, the quadrupole coupling constant might be small enough to observe ^{1}H–^{59}Co spin-spin coupling. Coordination of pyridine would cause an increase in the covalency of the cobalt(III)–carbon bond and in turn the field gradient becomes so strong as to yield complete decoupling in the present system. It would be of great use to elucidate the mechanism of the line broadening in respect of the controversial problems related to the nature of Co–carbon bonds in vitamin B_{12}.[31–33]

Figure 2 shows the spectra of Co(OEP)·CH_2CH_2-CO_2Et **3** and Co(OEP)·$CH_2CH_2CH_2COCH_3$ **15** in the high field region. Again signals due to the C_α-hydrogens are broad and overlapped by a less resolved peak due to C_β-hydrogens. In the presence of pyridine, **3** shows a sharp multiplet at τ 14.34, typical of AA'BB' pattern,[34] for the protons (C_α–H and C_β–H) while **15** showed a

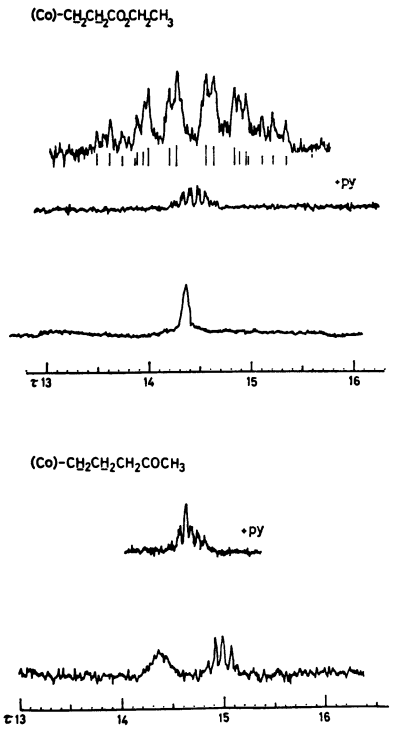


Fig. 2. 100 MHz NMR spectra of **3** and **15** in the high field region (measured in $CDCl_3$).

multiplet at ≈14.70 associated with C_α- and C_β-protons. The AA'BB' type splitting may arise from the exclusive presence of a rotational conformer as reported in 1,2-disubstituted ethane.[34,35]

Of the organocobalt(III)(OEP) complexes some, **3**,**5**—**9**, show double quartets due to the methylene protons of the peripheral ethyl groups of porphyrin, even though the difference in chemical shifts between the two quartets is quite small. Axial ligation of some unsaturated organic group forms a different magnetic anisotropic effect above and below the macrocyclic plane (diastereotopism).[36] The ratio of intensity for the two quartets is almost unity. Therefore, four of the methylene groups and the rest of four methylenes experience the different magnetic anisotropy due to the five coordinated metalloporphyrin. Free rotation of peripheral ethyl groups around the bond between the CH_2 and porphyrin carbon atom seems to be restricted to some extent due to the crowding of the ethyl groups.

Experimental

Spectral Measurements. Visible spectra (340—700 nm) were obtained in chloroform using a Hitachi EPS-3T spectrophotometer, and infrared spectra (4000—400 cm^{-1}) were determined in a KBr disk with a Hitachi-G3 spectrophotometer. NMR spectra were taken on Varian HA-100 and HR-220 spectrophotometers. All NMR spectra except for Co(I)(OEP) were recorded with deuteriochloroform as solvent and tetramethylsilane as internal standard. Pyridine was dried and distilled prior to use.

Reaction of Co(I)(OEP) with Organic Halides. A General Procedure: Co(II)(OEP) (100 mg) and sodium amalgam (2%, 3.0 g) were placed in a two necked flask (50 ml). The center neck was connected to a high vaccum tap and another neck was connected *via* a high vaccum tap to a 25 ml flask. Dry tetrahydrofuran (30 ml) was introduced to the flask and the solution was deareated by a repeated freeze-thaw method, and then stirred magnetically overnight. The color of the solution changed from reddish purple to lustrous orange-red. After the solution was transfered through a glass filter to the 25 ml flask, an excess of degassed alkyl halide (methyl iodide, ethyl iodide, ethyl 2-bromopropionate, *trans*-β-bromostyrene, or 2-bromoethylamine) was added, and then the solution was stirred for 10 min in the absence of light. The color of the solution changed to dark red. Methylene chloride (15 ml) was added to the reaction mixture and the solution was then

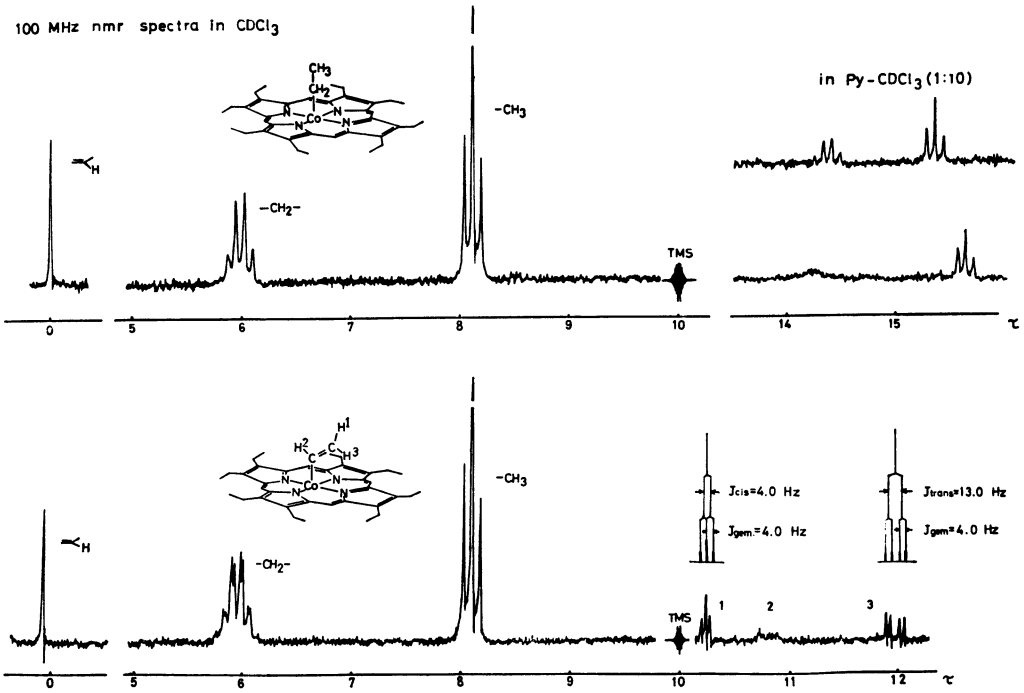


Fig. 3. 100 MHz NMR spectra of **2** and **7** measured in $CDCl_3$.

poured into 200 ml of cold water. The organic layer was separated, successively washed with water (200 ml × 3), and dried over Na_2SO_4. The solvent was removed at room temperature under reduced pressure and the residue was chromatographed on thin layer silica gel with benzene–methylene chloride (Merck, 60 PF_{254}, 20 × 20 × 0.1 cm^{-1}). The reddish orange zone was separated and extracted with methylene chloride. The solvent was removed and recrystallization of the residue afforded alkylcobalt(III)(OEP).

Co(OEP)·CH_3: This was eluted with methylene chloride–petroleum ether (1:3). Recrystallization from methylene chloride–petroleum ether afforded purple prisms (67 mg, 65%).

Co(OEP)·CH_2CH_5: This was eluted with methylene chloride–petroleum ether (1:5). Recrystallization from methylene chloride–petroleum ether afforded purple crystals (63 mg, 60%).

Co(OEP)·$CH_2CH_2CO_2Et$: Elution was carried out with methylene chloride–hexane (1:3). Recrystallization from methylene chloride–acetone gave purple crystals (50 mg, (42.7%).

trans-*Co(OEP)·CH=CHPh*: Eluent: methylene chloride–petroleum ether (1:3). Recrystallization from methylene chloride–petroleum ether afforded purple crystals (67 mg, 57%).

Co(OEP)·$CH_2CH_2NH_2$: β-Bromoethyl amine was prepared prior to use by treating its hydrogen chloride salt with an equimolar amount of triethylamine. The purification procedure is the same as that described above except that the organic layer was washed with diluted hydrobromic acid (200 ml × 5). Elution was carried out with methylene chloride–methanol (10:1). Recrystallization from methylene chroride–petroleum ether afforded dark purple crystals (43 mg, 40%).

Reaction of Co(I)(OEP) with Olefins, Acetylenes and Three Membered Ring Compounds. A General Procedure: An excess molar amount of the substrate was added to (acrylonitrile, ethyl acrylate, phenylacetylene, ethylene imine or cyclopropyl methyl ketone) or bubbled into (acetylene and ethylene oxide) the THF solution of Co(I)(OEP) prepared from 100 mg of Co(II)(OEP) as described above. The reaction mixture was stirred for 15 min and then a portion of 0.5 M NaOH was poured into the reaction vessel. Stirring was continued until the solution turned dark red (10—30 min). The succeeding procedures for separation and purification of the products are identical with those described in the reaction with alkyl halides.

Co(OEP)·CH_2CH_2CN: Eluted with methylene chloride–petroleum ether (1:3). Recrystallization from methylene chloride–petroleum ether affords purple crystals (50 mg, 44%).

Co(OEP)·$CH_2CH_2CO_2Et$: The products are identical with those prepared from ethyl 2-bromopropionate as described above (35 mg, 30%).

Co(OEP)·$CH{=}CH_2$: Thin layer chromatography of the reaction mixture on silica gel indicated that Co(II)(OEP) was formed together with alkyl cobalt complexes. Highly insoluble Co(II)(OEP) was removed by filtration before the separation by TLC was carried out. Recrystallization from methylene chloride–petroleum ether yielded vinyl cobalt(III)(OEP) (18 mg, 19%).

cis-*Co(OEP)·CH=CHPh and Co(OEP)·PhC=CH_2*: Monitoring reaction procedure by means of TLC showed that Co(II)(OEP) had generated during the reaction together with vinyl complexes. Elution was carried out with methylene chloride–hexane (1:5). Recrystallization from methylene chloride–acetone gave a mixture of *cis*-Co(OEP)·CH=CHPh and Co(OEP)·PhC=CH_2 (3:1) (34 mg, 29%). The deuteration experiment was carried out according to the general procedures described above except an addition of deuterium oxide solution of NaOD in place of aqueous NaOH solution.

Co(OEP)·CH_2CH_2OH: Eluent chloroform–hexane (1:2). Recrystallization from chloroform–hexane gave purple crystals (72 mg, 67%).

Co(OEP)·$CH_2CH_2NH_2$: The products are identical with those obtained in the reaction of Co(I)(OEP) with 2-bromoethylamine (35 mg, 33%).

Co(OEP)·$CH_2CH_2CH_2COCH_3$: Elution was carried out with methylene chloride–petroleum ether (1:3). Recrystallization from methylene chloride–petroleum ether gave 50 mg of deep purple crystals (44%).

Reaction with Carboethoxycyclopropane. The method used is entirely analogous to that described in the reaction with cyclopropyl methyl ketone. The main zone separated from TLC gave chloromethyl derivative, Co(OEP)·CH_2Cl. Recrystallization from methylene chloride–acetone gave 87 mg of deep purple crystals (79.8%). A minor zone gave an alkyl derivative (2 mg) with carbonyl stretching band at 1720 cm^{-1}.

Reaction with Cyanocyclopropane. The reaction mixture was stirred for 30 min. Co(OEP)CH_2Cl was obtained (31 mg, 37.5%).

Analytical data for the alkylcobalt(III)(OEP) complexes are given in Table 1. Visible and characteristic infrared data are listed in Table 2 and NMR data in Table 3. All reactions and manipulations involving cobalt(I) complexes were performed entirely under an atmosphere of purified argon. A 2% sodium amalgam was prepared by addition of mercury to the melted sodium metal in toluene. All procedures involving alkylcobalt(III) complexes were carried out in the dark whenever possible.

Intramolecular Methyl Migration. *N*-methyloctaethylporphyrinatocobalt(II) acetate [Co(*N*-MeOEP)]$^+OAc^-$ was prepared by a usual method[22] from Co(II) acetate and *N*-methyloctaethylporphyrin.[37] 80 mg of *N*-methyloctaethylporphyrinatocobalt(II) acetate was dissolved in THF and air was purged by argon. 10 mg of $NaBH_4$ in aqueous sodium hydroxide solution (0.5 M 0.5 ml) was added to the solution and the reaction mixture was stirred for 35 min. The color of the solution changed from dark green to dark red. Ten ml of methylene chloride was added to the solution and washed with water, and dried over Na_2SO_4 and evaporated. The resulting residue was chromatographed on silica gel (TLC 20 × 20 × 0.1 cm) with methylene chloride–petroleum ether (1:3). Recrystallization from methylene chloride–petroleum ether afforded deep purple crystals (42 mg, 57.6%).

Reaction of Co(III)(OEP)Br·py with Methyllithium. To 100 mg of pyridinobromocobalt(III)octaethylporphyrin[21] dissolved in anhydrous dimethoxyethane was added an equimolar amount of methyllithium prepared from methyl iodide and lithium metal under nitrogen. The reaction was monitored by TLC (silica gel). After the reaction was completed, the reaction mixture was poured into 200 ml of water, washed with water several times and dried over Na_2SO_4. The succeeding procedures are identical with those described above. Recrystallization from methylene chloride–petroleum ether afforded Co(OEP)–CH_3 (72 mg, 55%).

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