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The Spectroscopic Properties and Organometallic Reactivities of Cobalt(III) Porphyrins

Jun-ichiro Setsune,* Yasushi Saito,† Yoshihiro Ishimaru,
Mitsuhiro Ikeda,† and Teijiro Kitao†
Department of Chemistry, Faculty of Science,
Kobe University, Nada, Kobe 657
† Department of Applied Chemistry, College of Engineering,
University of Osaka Prefecture, Sakai, Osaka 591
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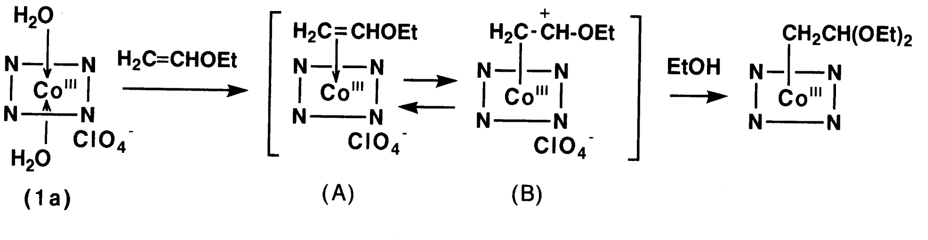
Chlorocobalt(III) porphyrins showed novel UV-vis and ^{1}H NMR spectra in a non-coordinating solvent to suggest displacement of the cobalt out of the porphyrin plane toward the axial ligand in solution. They underwent insertion of alkynes into the Co–Cl bond to generate σ-(*trans*-2-chlorovinyl)cobalt(III) complexes. In a special case, novel [4+2]cycloaddition reaction between the Co–N–C(pyrrole-α)–C(*meso*) moiety of [Co^{III}Cl(oep)] [oep=octaethylporphyrin dianion] and dimethyl acetylenedicarboxylate took place. The reaction behavior of chlorocobalt(III) porphyrins was compared with that of diaquaperchloratocobalt(III) porphyrins which also reacted with alkynes in the presence of 2,6-lutidine to give analogous σ-vinylcobalt(III) porphyrins with a 2,6-dimethyl-1-pyridinio substituent occupying the *trans*-β-position of the σ-vinyl group. While the methoxycarbonyl group of methyl propiolate was directed to the α side of these σ-vinylcobalt(III) complexes, the phenyl group of phenylacetylene was found to be directed to the α side of σ-(2-chlorovinyl)cobalt(III) porphyrin and to the β side of σ-[2-(2,6-dimethyl-1-pyridinio)vinyl]cobalt(III) porphyrin.

Studies on the reactions of trivalent cobalt and rhodium complexes with unsaturated compounds have been stimulated by a hypothesis that a Co(III) π-complex intermediate may play a key role in the coenzyme B$_{12}$ dependent rearrangement of ethylene glycol to acetaldehyde.[1] A metal π-complex with a metal in a high oxidation state is in itself of great interest in view of the fact that a metal is in a low oxidation state in ordinary metal π-complexes.[2] It was shown that reaction of [Co^{III}(ClO$_4$)(oep)(H$_2$O)$_2$] [oep=octaethylporphyrin dianion] (**1a**) with ethyl vinyl ether gave a σ-alkylcobalt(III) porphyrin.[1a] A metal π-complex intermediate (**A**) in which an electron-rich alkene coordinates to a high valent metal complex was postulated in this type of reaction and the regiochemistry was interpreted in terms of a σ-alkyl carbonium ion intermediate (**B**) as shown in Scheme 1. The high reactivity of **1a** as an electrophilic center is expected from its novel spectroscopic property which was explained in terms of the reversible formation of a Co(II) porphyrin π-cation radical in non-coordinating solvents.[3] However, the reaction behaviors and the spectroscopic properties of [Co^{III}Cl(oep)] (**1b**) have never been elucidated. We have recently shown that Co^{III}(oep) undergoes novel insertion of dimethyl acetylenedicarboxylate (DMAD) between the cobalt and the porphyrin nitrogen or the porphyrin *meso* carbon (C-5, 10, 15, 20) depending on whether the counter anion of Co^{III}(oep) is perchlorate or chloride.[4] In this paper, we would like to make thorough description on the spectroscopic properties (^{1}H NMR and UV-vis) and organometallic reactivities (towards alkynes) of **1b** in comparison with those of **1a**.

Results and Discussion

Spectroscopic Properties of Co(III) Porphyrins. Yamamoto and co-workers have reported that ^{1}H NMR signals of [Co^{III}Cl(tpp)] (**1d**) [tpp=5,10,15,20-tetraphenylporphyrin dianion] become broadened as increasing temperature in tetrachloroethane.[5] According to their paper, signals due to the tpp ligand were only partially resolved even at room temperature with showing the magnetic moment of 1.7 BM in the solution. Addition of a small amount of methanol to **1d** in dry CH$_2$Cl$_2$ caused UV-vis spectral change as shown in Fig. 1 (top).[6] These spectral properties of **1d** in non-coordinating solvents are explainable in terms of the five-coordinate structure in which the Co(III) ion is displaced out of the porphyrin plane. Although the X ray crystal structure of **1d** was reported to show that the cobalt was in the mean plane of porphyrin four nitrogens,[7] it has



Scheme 1.

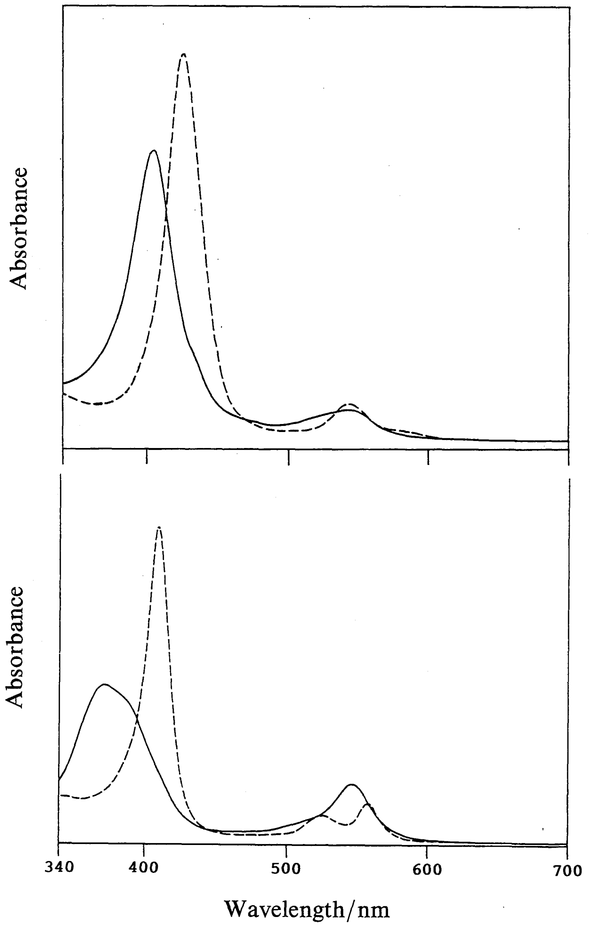


Fig. 1. UV-vis spectra of $\mathrm{Co^{III}}$ porphyrins in CH_2Cl_2 (solid line) and after addition of a drop of MeOH (dashed line); [$\mathrm{Co^{III}}$Cl(tpp)] (**1d**) [top] and [$\mathrm{Co^{III}}$Cl(oep)] (**1b**) [bottom].

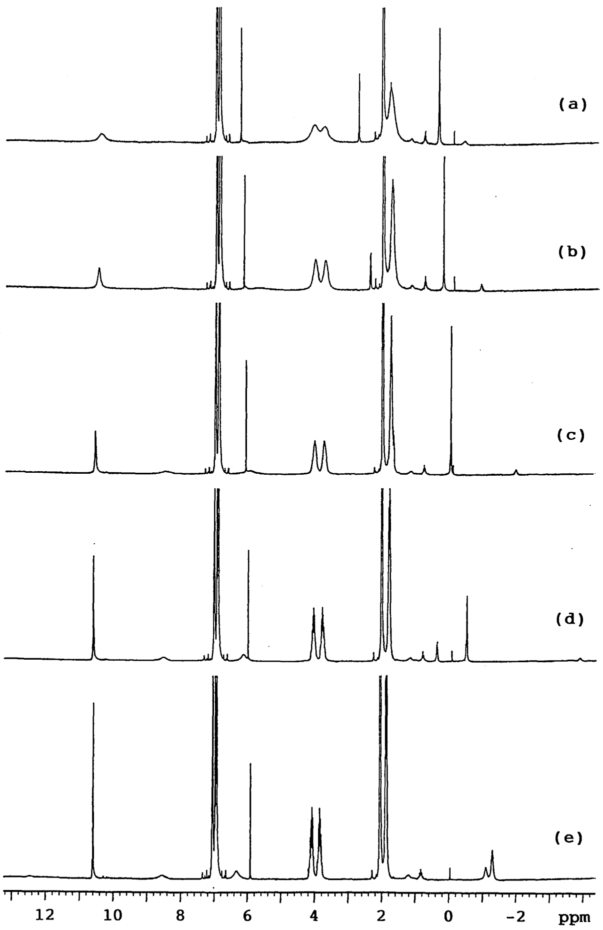


Fig. 2. Variable temperature ^{1}H NMR spectra of [$\mathrm{Co^{III}}$Cl(oep)] (**1b**) in C_7D_8 at 60 (a), 40 (b), 20 (c), 0 (d), −20 °C (e).

recently been suggested by the same authors that water might be occupying the sixth coordination site in the original crystal of **1d**.[8] It is well known that spin state of iron(III) porphyrins is dependent on the molecular structure. That is, high spin (S=5/2) state is favored in the five-coordinate [$\mathrm{Fe^{III}}$Cl(por)] in which iron is 0.5 Å above the mean plane of porphyrin nitrogens, whereas six-coordinate [$\mathrm{Fe^{III}(L)_2}$Cl(por)] is of a low spin state (S=1/2) without deviation of the iron.[9] Thus, a high spin state would be preferable in this five-coordinate structure to account for the greater paramagnetic contribution of **1d** at the higher temperatures.

We have measured ^{1}H NMR and UV-vis spectrum of **1b** in this work. Compound **1b** showed an unusual UV-vis spectrum in dry CH_2Cl_2 with a remarkably reduced ratio of the Soret band intensity with respect to the visible band intensity as shown in Fig. 1 (bottom). However, this spectrum changed to an ordinary d^6 low spin metallooctaethylporphyrin-spectrum with a sharp Soret and two visible bands by adding a drop of methanol. The ^{1}H NMR signals of **1b** in toluene-d_8 were made broader with raising temperature from −20 °C to 60 °C as shown in Fig. 2. Although this temperature dependence of **1b** is analogous to the case of **1d**, a stronger ligand field of oep than tpp makes the high spin state of $\mathrm{Co^{III}}$(oep) less accessible if spin state equilibrium is responsible for these unusual spectroscopic properties. Therefore, a diamagnetic sharp ^{1}H NMR spectrum was observed for **1b** at room temperature in $CDCl_3$ as depicted in Fig. 3, where the signals due to diastereotopic methylene protons of the peripheral ethyl groups were observed as two discrete multiplets centered at $\delta = 3.92$ and 4.43. The unusual chemical shift difference of 0.51 ppm in $CDCl_3$ for **1b** indicates that the magnetic circumstance of one side of the porphyrin plane of **1b** is so much different from the other side as in the case of metallooctaethylporphyrins with two cofacial porphyrin ligands {e.g. [Ce(oep)$_2$], [Mo_2(oep)$_2$], and [Rh_2(oep)$_2$]},[10–12] since the latter compounds show a similar chemical shift difference of ca. 0.5 ppm. Aluminum(III), gallium(III), indium(III), and thallium(III) octaethylporphyrins were reported to show the methylene proton NMR signals with a ABX_3

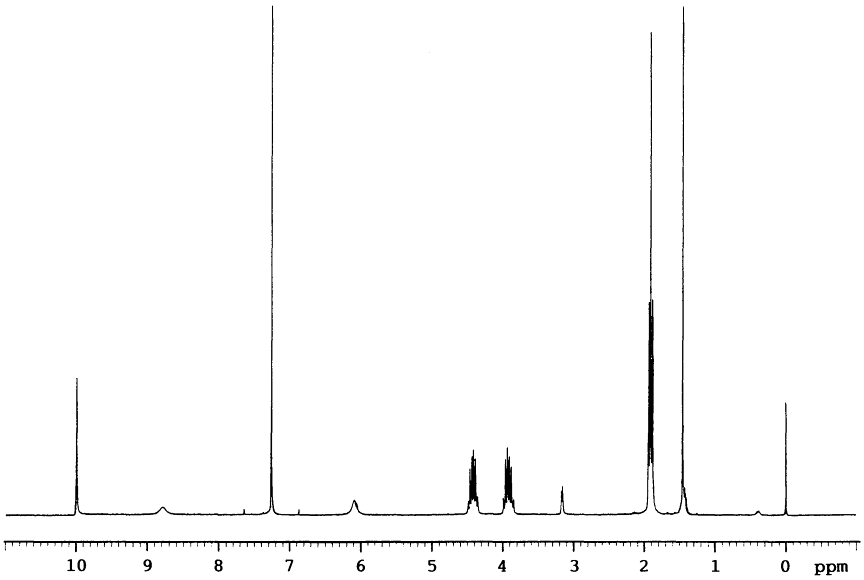
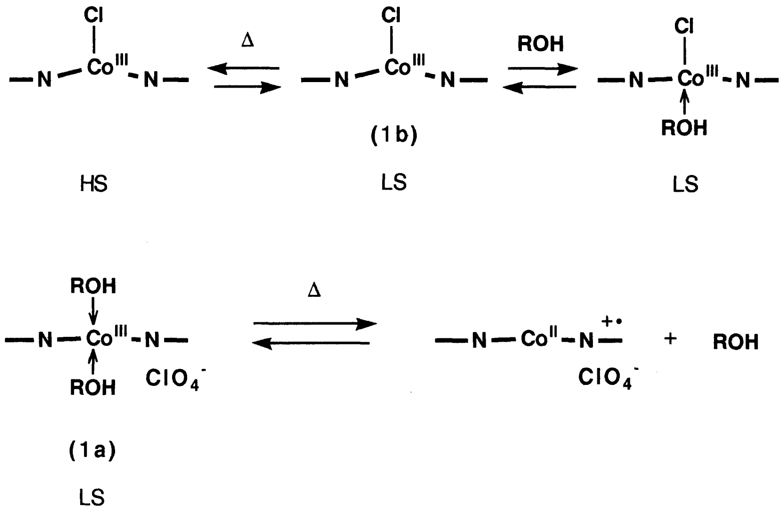


Fig. 3. ^{1}H NMR spectrum of **1b** in $CDCl_3$ at 22 °C.



Scheme 2.

pattern and this magnetic anisotropy was ascribed to the out-of-plane displacement of the metal.[13] However, the chemical shift differences of the diastereotopic methylene protons of these group 13 metalloporphyrins are always around 0.1 ppm. Although the chemical shift difference of the diastereotopic methylene protons of **1b** was not so large in toluene-d_8 ($\Delta\delta$=0.25 at 0 °C) as in $CDCl_3$, this value is still remarkable. A chlorine atom axially bonded to cobalt is not in itself responsible for this magnetic anisotropy because [Rh^{III}Cl(oep)] does not show appreciable separation of the diastereotopic methylene proton signals.[14] Furthermore, the molecular weight measurement by the vapor-pressure osmometry did not show any sign of aggregation for **1b** in dry CH_2Cl_2 solution (550 observed; 627 in theory). Therefore, these unusual ^{1}H NMR and UV-vis spectral features would be attributable to the deviation of the Co ion out of the porphyrin plane (see Scheme 2).

It has recently been reported that **1a** shows very broad visible bands characteristic of π-cation radicals in CH_2Cl_2 at room temperature instead of typical d^6 low spin Co(III) porphyrin spectra in CH_2Cl_2 at low temperature or in coordinating solvents.[3] We have measured variable temperature ^{1}H NMR spectra of **1a** in CD_2Cl_2 along with [Co^{III}(ClO_4)(ttp)(H_2O)$_2$] [ttp = 5,10,15,20-tetra-*p*-tolylporphyrin dianion] in $CDCl_3$, as shown in Fig. 4. The observed temperature dependency in the ^{1}H NMR spectra parallels the temperature dependent UV-vis spectral change reported previously.[3] That is, diamagnetic ^{1}H NMR signals due to the porphyrin ligand

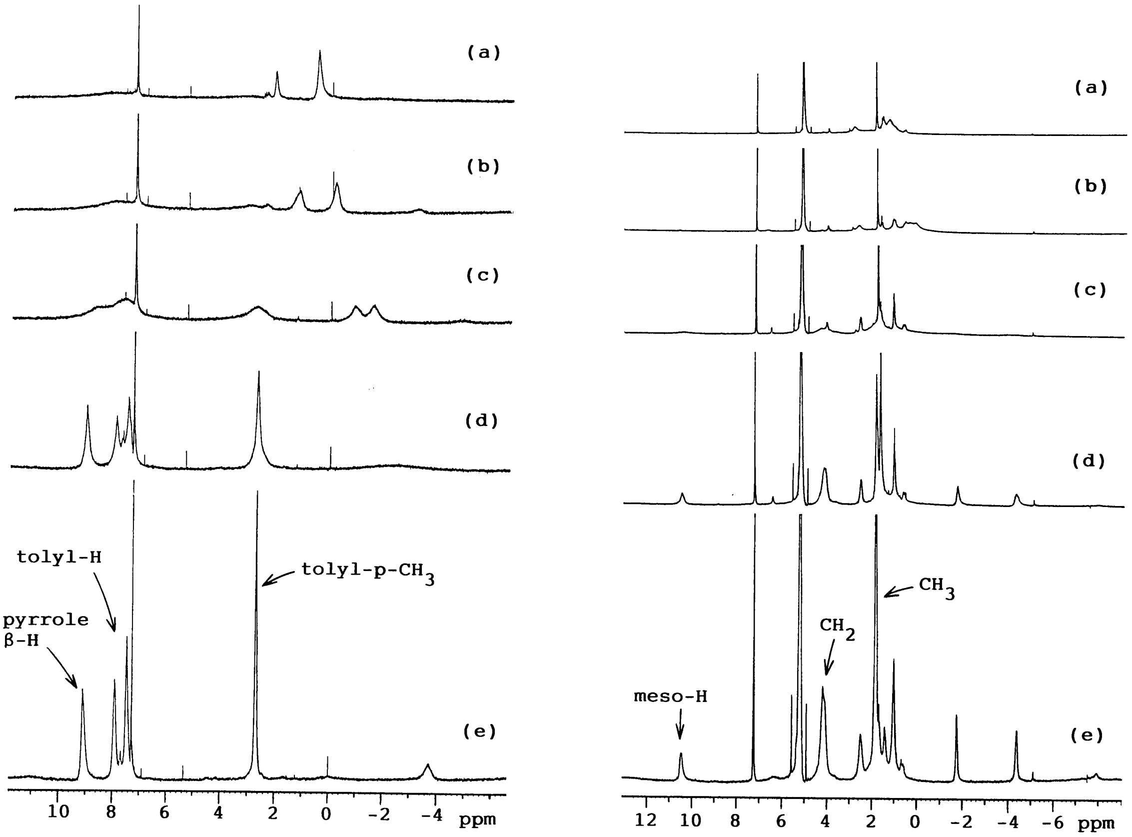
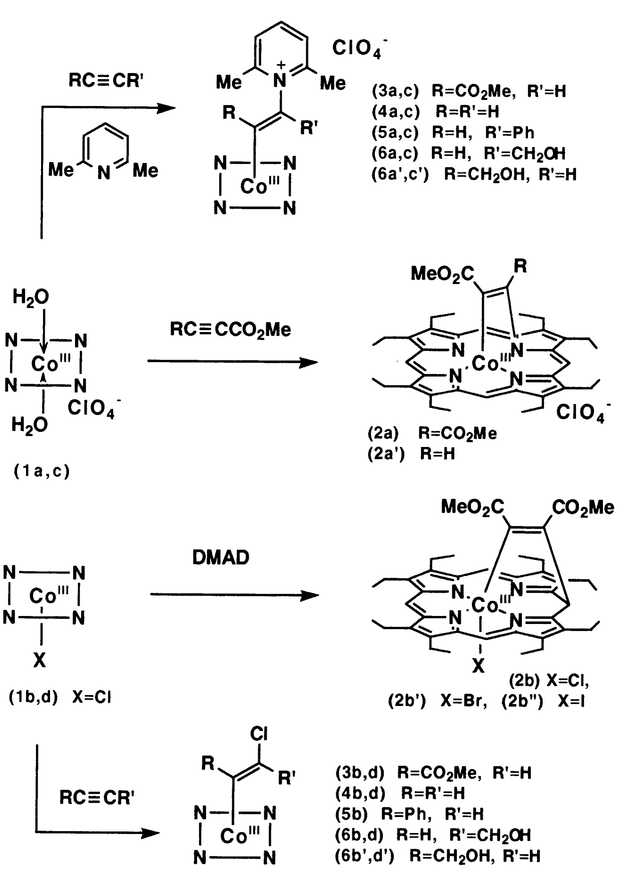


Fig. 4. Variable temperature ^{1}H NMR spectra of [Co^{III}(ClO$_4$)(ttp)(H$_2$O)$_2$] in CDCl$_3$ at 25 (a), 10 (b), −10 (c), −30 (d), −50 °C (e) [left], and [Co^{III}(ClO$_4$)(oep)(H$_2$O)$_2$] (**1a**) in CD$_2$Cl$_2$ at 0 (a), −30 (b), −50 (c), −70 (d), −90 C (e) [right].

of **1a** became observable below −50 °C, at which temperature is apparent typical d^6 low spin Co(III) porphyrin UV-vis spectrum. However, the methylene proton signal of **1a** at 4 ppm did not show such a remarkable splitting as the diastereotopic methylene signals for **1b**. While Co(II) porphyrin π-cation radical structure was suggested for the perchlorate **1a** in CH$_2$Cl$_2$ on the basis of UV-vis and resonance Raman evidence,[3] UV-vis and ^{1}H NMR spectral features of the chloride **1b** in comparison with those of the perchlorate **1a** are indicative of deviated five-coordinate structure for **1b**.

Reactions of [Co^{III}Cl(oep)] with DMAD. We have recently demonstrated that organocobalt(III) complexes (**2a**, **2a′**, **2c**, **2c′**) with novel Co,N-bridged structure are formed by the reaction of **1a** and [Co^{III}(ClO$_4$)(tpp)(H$_2$O)$_2$] (**1c**) with DMAD and methyl propiolate in CH$_2$Cl$_2$.[4] In contrast to the perchlorate **1a**, the chloride **1b** gave a Co,C$_{meso}$-bridged organocobalt(III) complex (**2b**) in 82% yield under similar reaction conditions to those for **2a**. The reaction of [Co^{III}Br(oep)] and [Co^{III}I(oep)] with DMAD also occurred to give similar Co,C$_{meso}$-bridged organocobalt (III) complexes (**2b′**) and (**2b″**), respectively (see Scheme 3). The UV-vis absorption bands at 349 and 477 nm with relatively low extinction coefficients (ca. 20000) of **2b** are quite different from those of porphyrin



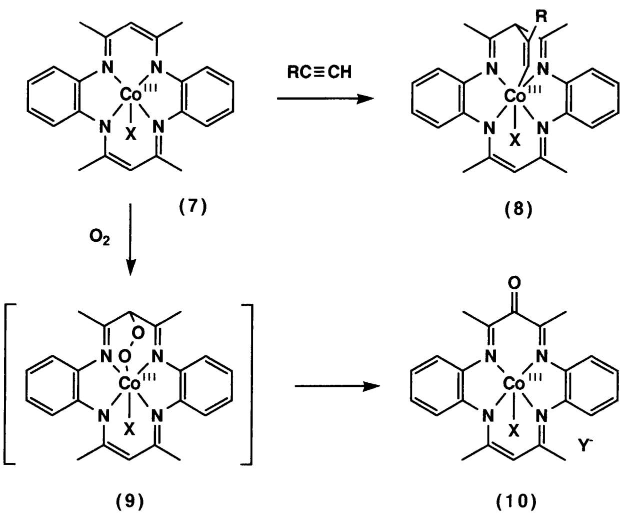
Scheme 3.

compounds including Co,N-bridged porphyrin **2a**. ^{1}H and ^{13}C NMR spectrum of **2b** are indicative of C_s molecular symmetry with a mirror plane containing a C(5)–Co–C(15) axis. The ^{1}H chemical shifts of the *meso* protons (6.39, 6.20, and 6.15 ppm) are shifted by ca. 4 ppm to the higher field than those of **2a** and one of the ^{13}C signal due to the *meso* carbons appears at an aliphatic carbon region (45.8 ppm) whereas the others resonate at 121.9 and 118.3 ppm. These data are consistent with the structure in which saturation occurs at the C(5) *meso* position. The ^{13}C signal at 141.1 ppm is associated with the vinylic carbon (derived from DMAD acetylenic carbons) bonded to the saturated C(5) *meso* position. The remaining vinylic carbon should be σ-bonded to cobalt and so it was not observed due to the quadrupolar relaxation effect of Co nucleus ($I=7/2$).[4)]

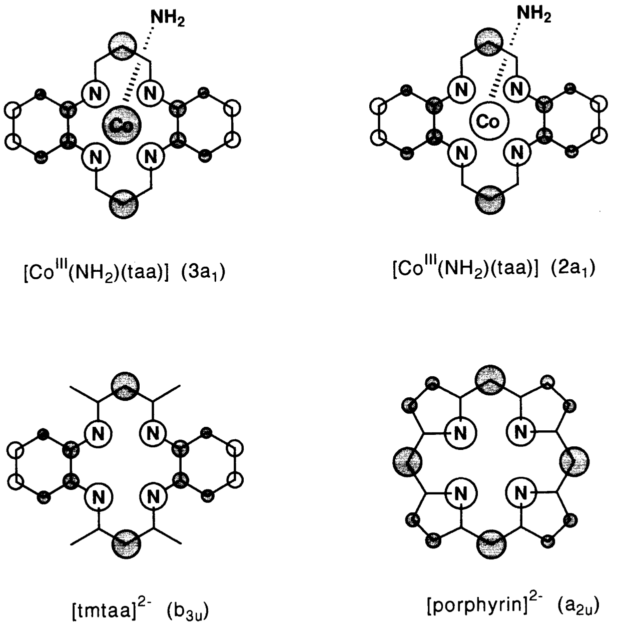
The reactivity of Co^{III}(oep) complexes toward DMAD increased with decreasing electron donation from the axial ligands (I > Br > Cl > H_2O) as shown in Table 1. The five-coordinate structure of **1b** in dry CH_2Cl_2 would be responsible for this novel [4+2]cycloaddition reaction between the Co–N–C(pyrrole-α)–C(*meso*) moiety and a C–C triple bond, since **1b** and DMAD did not react at all in ethanol where six-coordination is predominant. A similar [4+2]cycloaddition reaction was reported to occur when Co(III) complex (**7**) of 5,7,12,14-tetramethyl-2,3:9,10-dibenzo-1,4,8,11-tetraaza[14]annulene (tmtaa) was allowed to react with alkynes (see Scheme 4).[15)] A theoretical study on the interaction of the model complex Co^{III}(NH$_2$)(taa) [taa=2,3:9,10-dibenzo-1,4,8,11-tetraaza[14]annulene] for **7** with acetylene pointed out that the energy minimum was reached at the orientation where the C–C bond of acetylene is aligned with the C(6)–C(13) axis of the macrocycle and slipped off from η^2 coordination toward η^1 coordination with the terminal acetylene carbon interacting with the C(6) position.[16)] In this orientation, acetylene π and π* orbitals can overlap with the LUMO ($3a_1$) and the HOMO ($2a_1$), respectively, of the five-coordinate Co(III) macrocycle which are constructed from the macrocycle HOMO (b_{3u}), the metal d_{z^2} and p_z orbitals, and the σ-orbital of the axial fifth ligand. These $3a_1$–π and $2a_1$–π* interactions are possible because the macrocycle b_{3u} orbital has large lobes at the C(6) and C(13) positions besides at the nitrogens. Since the macrocycle HOMO (b_{3u}) is analogous to the porphyrin HOMO (a_{2u}) in the sense that the 4 nitrogens and the C(6) position (which corresponds to the *meso* position for porphyrin) have large lobes with opposite signs as shown in Scheme 5, it would be expected that analogous orbital correlation holds for the interaction of **1b** with DMAD. The porphyrin a_{1u} orbital which is energetically very close to the a_{2u} orbital would not be important in the reactions where a nitrogen or a *meso* carbon is involved, because it has no lobe at the nitrogens and the *meso* carbons. It should not be overlooked that the saddle shape structure of the macrocyclic ligand of **7** allows effective overlap of the acetylene orbitals with the Co macrocycle orbitals especially at the C(6) position. The reactivity at the *meso* position of Co(III) porphyrin would be enhanced by a similar structural deformation such as a doming of a porphyrin plane.

Table 1. Reaction of [Co^{III}X(oep)] with DMAD

X	Solvent	Temp. °C	Time h	Yield %
Cl	CH_2Cl_2	38	24	82
Br	CH_2Cl_2	38	40	88
	$CHCl_3$	64	2	89
	C_2H_5OH	78	48	0
I	$C_2H_4Cl_2$	80	48	51
Me	$C_2H_4Cl_2$	80	48	0



Scheme 4.



[Co^{III}(NH$_2$)(taa)] ($3a_1$)

[Co^{III}(NH$_2$)(taa)] ($2a_1$)

[tmtaa]$^{2-}$ (b_{3u})

[porphyrin]$^{2-}$ (a_{2u})

Scheme 5.

Table 2. Reaction Conditions, Yields, and ^{1}H NMR Data of σ-(Vinyl)Co^{III} Porphyrins

Alkyne	Time	Prod.	Yield	^{1}H NMR chemical shifts (δ-value in CDCl$_3$)						
	h		%	*meso*	CH$_2$	CH$_3$	α[a]	β[a]	*R*[b]	2,6-Lutidine
HC$_2$CO$_2$Me	1	**3a**	77	10.33	4.08	1.88	—	−1.22	1.44 (s)	0.09 (s), 6.54 (d), 7.32 (t)
C$_2$H$_2$	1	**4a**	64	10.24	4.06	1.87	0.01	−0.87 (J=13.0)		−0.06 (s), 6.61 (d), 7.36 (t)
HC$_2$Ph	1	**5a**	50	10.07	3.99	1.84	−0.51	—	3.40 (d), 6.55 (t), 6.86 (t)	0.20 (s), 6.77 (d), 7.59 (t)
HC$_2$CH$_2$OH	1	**6a**	30	10.27	4.07	1.87	−0.89	—	−2.47 (d), −1.03 (t)	0.13 (s), 6.51 (d), 7.22 (t)
		6a′		10.15	4.03	1.84	—	−1.99	−0.68 (d), 0.77 (t)	0.16 (s), 6.50 (d), 7.22 (t)
HC$_2$CO$_2$Me	24	**3b**	57	10.30	4.06	1.92	—	−2.09	1.82 (s)	
C$_2$H$_2$	1	**4b**	41	10.16	4.03	1.90	−0.94	−1.63 (J=11.6)		
HC$_2$Ph	2	**5b**	30	10.12	4.00	1.87	—	−2.20	2.51 (d), 5.81 (t), 6.37 (t)	
				β-py[c]	phenyl		α[a]	β[a]	*R*[b]	2,6-Lutidine
HC$_2$CO$_2$Me	1	**3c**	58	8.98	8.16	7.79	—	−0.21	1.70 (s)	0.39 (s), 6.62 (d), 7.38 (t)
C$_2$H$_2$	1	**4c**	14	8.95	8.11	7.77	0.56	−0.06 (J=13.1)		0.27 (s), 6.70 (d), 7.40 (t)
HC$_2$Ph	1	**5c**	34	8.89	8.02	7.77	0.20	—	3.70 (d), 6.73 (t), 6.95 (t)	0.49 (s), 6.94 (d), 7.72 (t)
HC$_2$CH$_2$OH	1	**6c**	9	8.95	8.10	7.77	−0.31	—	−1.80 (d), 0.24 (t)	0.49 (s), 6.62 (d), 7.32 (t)
		6c′		8.97	8.10	7.77	—	−1.42	−0.15 (d), 1.64 (t)	0.43 (s), 6.62 (d), 7.32 (t)
HC$_2$CO$_2$Me	24	**3d**	31	8.90	8.13	7.75	—	−1.42	1.98 (s)	
C$_2$H$_2$	1	**4d**	45	8.87	8.11	7.77	−0.49	−1.01 (J=11.5)		
HC$_2$CH$_2$OH	2	**6d**	45	8.90	8.08	7.73	−0.77	—	−0.42 (d), 1.45 (t)	
		6d′		8.97	8.10	7.77	—	−1.64	−1.71 (d), −2.79 (t)	

a) α and β denote Co–CH= and Co–C=CH– proton, respectively. b) Protons due to substituents on the σ-vinyl group. c) β-Pyrrole protons.

The ligand oxidized product (**10**) was produced from **7** and a epidioxy type intermediate (**9**) was postulated as a result of similar cycloaddition of **7** with molecular oxygen instead of alkyne.[15] Although *meso*-oxidation of **1b** with molecular oxygen did not take place, the Co,C$_{meso}$-etheno-bridged complex **2b** is regarded as a model compound for the Fe,C$_{meso}$-epidioxy-bridged complex which might occur in the initial event of heme degradation to biliverdins catalyzed by heme oxygenase. We would like to point out the possibility that heme oxygenase cause deformation of a porphyrin ring and raises reactivity of the *meso* position with dioxygen.

Reaction of Co(III) Porphyrins with Alkynes. While novel cycloaddition of DMAD with **1b** occurred as described above, other alkynes (methyl propiolate, acetylene, phenylacetylene, and propargyl alcohol) were inserted into a Co(III)–Cl bond of **1b** and **1d** in dry CH$_2$Cl$_2$ to give σ-(2-chlorovinyl)Co(III) porphyrin complexes (**3b**, **3d**, **4b**, **4d**, **5b**, **6d**) in moderate yields. Whereas the perchlorates, **1a** and **1c**, undergo insertion of DMAD and methyl propiolate into a Co(III)–N bond, analogous Co,N-bridged complexes have never been isolated unless alkynes are substituted with electron-withdrawing groups.[4b] On the other hand, the σ-vinylcobalt(III) complexes (**3a**–**6a** and **3c**–**6c**) were formed in moderate yields when the perchlorates were allowed to react with in the presence of 2,6-lutidine. 2,6-Lutidine was introduced into the *trans* β-position with respect to Co(III) in place of the chlorine in the complexes **3b**, **3d**, **4b**, **4d**, **5b**, **6d**.

The structure of these adduct complexes was determined on the basis of the ^{1}H (summarized in Table 2) and ^{13}C NMR data, UV-vis data, and microanalysis. ^{1}H–^{1}H Vicinal coupling constants (11—13 Hz) of the vinylic protons of **4a**, **4b**, **4c**, **4d** are indicative of *trans* addition to acetylene. Furthermore, similarity of the ^{1}H chemical shifts (−0.94 for α; −1.63 for β) due to the vinylic protons of **4b** with those (−1.48 for α; −1.79 for β) of σ-(*trans*-2-chlorovinyl)Rh^{III}(oep)[17] guarantees the σ-(*trans*-2-chlorovinyl)Co^{III} structure of **4b** taking into account of ca. 0.5 ppm lower field shift of the cobalt-bound vinylic proton than the rhodium-bound vinylic proton due to the more electronegative cobalt atom. The up-field shift of the 2,6-lutidine protons in the ^{1}H NMR of **3a**–**6a** and **3c**–**6c** along with the similarity of their chemical shifts is indicative of the *trans* addition of Co and 2,6-lutidine to alkynes in all these complexes. The regiochemistry of the addition of Co(III) and chlorine (or 2,6-lutidine) to methyl propiolate and phenylacetylene was determined on the basis of the ^{1}H–^{13}C coupling in the σ-vinyl moiety. Since the α-vinylic carbon bound to Co does not give ^{13}C absorption, signals observed at 115.8 ppm for **3a**, 128.5 for **5a**, 98.63 for **3b**, and 91.23 for **5b** were unambiguously assigned to the β-vinylic carbon. The vinylic protons of the axial organo groups of **3a**, **3b**, and **5b** which appeared at −1.22, −2.09, and −2.20 ppm, respectively, were found to be coupled with the ^{13}C signals due to the β-vinylic carbon, as shown in Fig. 5. However, the vinylic proton of **5a** at −0.51 ppm was not coupled to the β-vinylic carbon at 128.5 ppm. This means that the direction of addition of phenylacetylene to **1a** is different from that to **1b**, while a methoxycarbonyl group of methyl propiolate was directed to the cobalt side of both **3a** and **3b**.

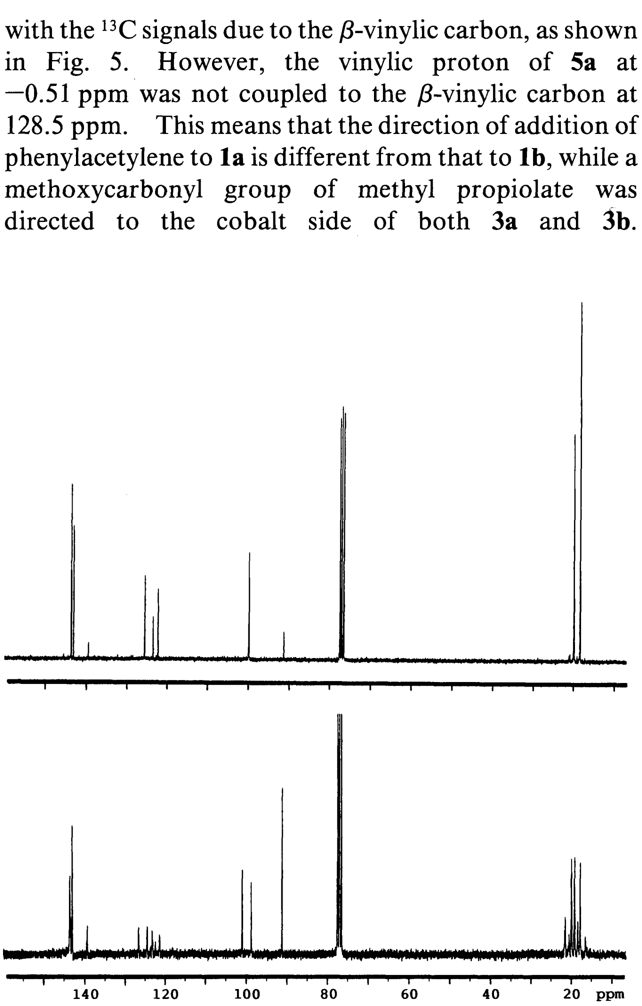


Fig. 5. ^{13}C NMR spectrum of **5b** in $CDCl_3$ with ^{1}H complete decoupling [top], and with ^{1}H selective decoupling at the vinylic proton chemical shift (−2.20 ppm) [bottom].

Comparison of the ^{1}H chemical shifts (especially of the ortho proton) of the phenyl substituent of **5a** and **5b** with those of σ-(*cis*-styryl), σ-(*trans*-styryl), and σ-(1-phenylvinyl) complexes of Co^{III}(oep)[18] and Rh^{III}(oep)[14,17] provides further evidence on the structure of their axial organo groups. The ortho proton chemical shifts of σ-(*cis*-styryl)Co^{III}(oep) (**11**) and its rhodium analogue (**11′**) are 3.90 and 3.73 ppm, respectively, while those of *trans* isomers (**12**) and (**12′**) are 4.90 and 4.69 ppm. That of σ-(1-phenylvinyl)Co^{III}(oep) (**13**) is 2.27 ppm. These are summarized in Fig. 6. Thus, ortho phenyl proton chemical shifts are diagnostic of the relative position of the phenyl group with respect to Co(III) porphyrin in the σ-phenylvinyl systems with various substituents at the vinylic positions. This is simply because the ortho-proton chemical shift depends not on the electronic effect of the substituents on the σ-vinyl group but on the ring current effect of porphyrin. The ortho-proton chemical shift (3.40 ppm) of **5a** is typical of σ-(*cis*-styryl) structure, and that (2.51 ppm) of **5b** is in the range of σ-(1-phenylvinyl) structure. These are in agreement with the result based on the ^{1}H–^{13}C coupling experiments. Since the *cis* and *trans* β-vinyl protons, with respect to cobalt, of **13** resonate at −2.67 and −0.85 ppm, respectively, the vinyl proton chemical shift (−2.20 ppm) of **5b** is associated with the *cis* site. This clearly indicates the *trans* addition of Co and Cl to phenylacetylene.

All the producuts obtained through the reaction with propargyl alcohol were found to consist of two isomeric σ-(vinyl)Co^{III} porphyrins in a ratio of ca. 1:1 on the basis of two sets of ^{1}H NMR absorptions.

As shown above, the reactions of Co(III) and Rh(III) porphyrins with alkynes are basically the same to lead to the addition of the electrophilic metal(III) porphyrin moiety and the nucleophilic chloride or 2,6-lutidine

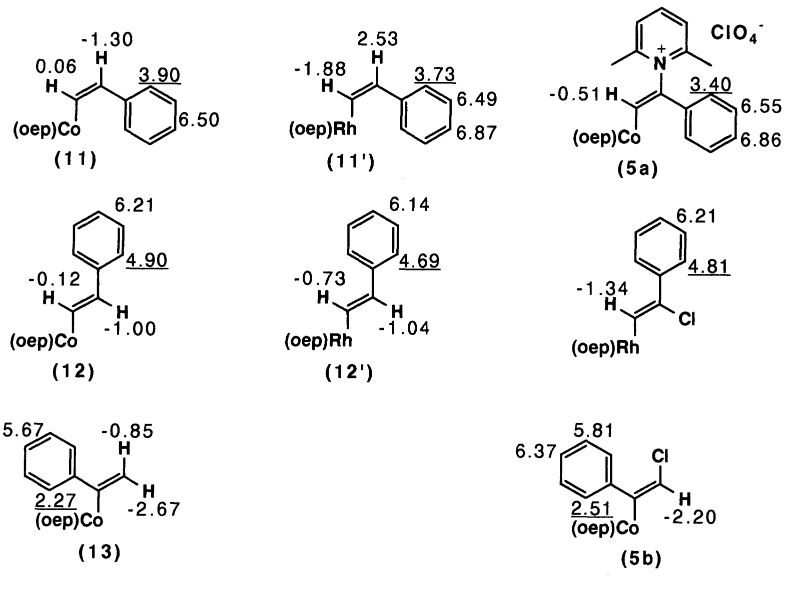
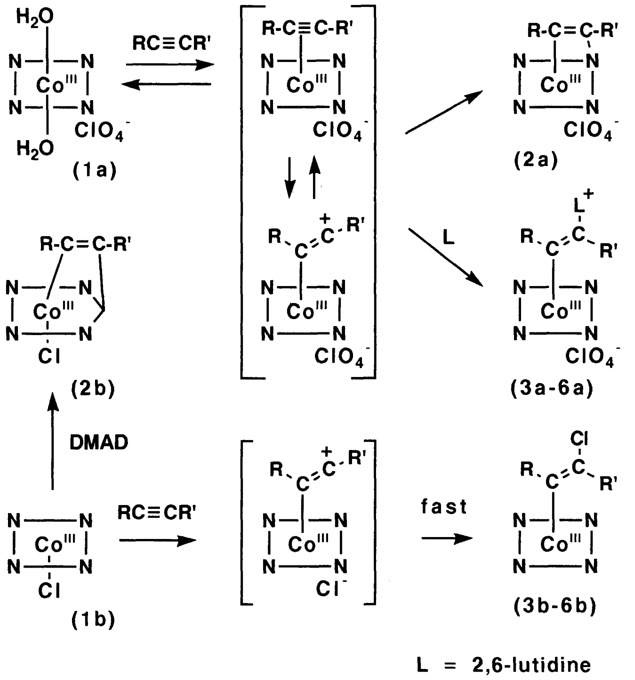


Fig. 6. ^{1}H-Chemical shifts of σ-(phenylvinyl)Co^{III}(oep) and σ-(phenylvinyl)Rh^{III}(oep) complexes (δ-value in $CDCl_3$).



Scheme 6.

across a carbon–carbon triple bond. Therefore, a polarized alkyne such as methyl propiolate gave the σ-(2-chlorovinyl)Co^{III} complexes **3a**, **3b**, **3c**, **3d** with a methoxycarbonyl group exclusively at the α-position. In contrast, the direction of the addition of **1b** to phenylacetylene is different from that of **1a** to phenylacetylene. Since a phenyl group can be regarded as an electron-withdrawing group, it should be directed to the cobalt side (α-side) as well as a methoxycarbonyl group if reaction is kinetically controlled. In the reaction of **1a**, weaker nucleophilic reactivity of 2,6-lutidine than chloride[19] allows reversible formation of an acetylene π-complex intermediate which is stabilized by σ-π rearrangement especially when a phenyl group is directed to the β-side as shown in Scheme 6. However, DMAD would not make effective π-coordination to Co(III) due to its low electron density. Therefore, [4+2]cycloaddition becomes the principal reaction course if a porphyrin ligand is deformed enough. On the other hand, **1a** was found to give the 2,6-lutidine adduct **3a** or the Co,N-bridged complex **2a** depending on whether 2,6-lutidine is present or not, when methyl propiolate was allowed to react. It was confirmed that 2,6-lutidine did not convert **2a** into **3a**. These observations are easily rationalized in terms of a common σ-vinyl carbonium ion intermediate which can be attacked by 2,6-lutidine nitrogen intermolecularly or porphyrin nitrogen intramolecularly as shown in Scheme 6. Since **1a** is more electropositive than **1b**, the π-coordination of DMAD to Co(III) of **1a** seems still important and result in the formation of a Co,N-bridged complex **2a** by way of a σ-vinyl carbonium ion intermediate.

In conclusion, the reaction of Co(III) porphyrins with alkynes gave various σ-vinylCo(III) porphyrins depending on the alkyne substituents, porphyrin substituents, axial ligands, and solvent. The formation of novel Co,C_{meso}-etheno-bridged porphyrin **2b** would be attributed to the five-coordinate structure of $[Co^{III}Cl(oep)]$ **1b**.

Experimental

UV-visible spectra were measured on a Shimadzu UV-240 spectrophotometer. ^1H NMR (270 MHz) and ^{13}C NMR (67.8 MHz) were recorded on a JEOL GX-270 spectrometer in CD_2Cl_2, $CDCl_3$, and C_7D_8. ^1H and ^{13}C chemical shifts are referenced with respect to tetramethylsilane (0 ppm) and $CDCl_3$ (77.05 ppm) as internal standards, respectively. Elemental analysis of C, H, N, was made with Yanaco CHN corder. Molecular weight was measured at 20 °C in CH_2Cl_2 on a Knauer vapor pressure osmometer. Kieselgel 60F_{254} silica gel plates (Merck) and Wakogel C-300 silica gel (Wako Junyaku) were used for TLC and column chromatography. Acetylene gas (99.99%) was supplied from Nichigo acetylene Co., Ltd. Japan. $[Co^{III}(ClO_4)(oep)(H_2O)_2]$ (**1a**), $[Co^{III}(ClO_4)(tpp)(H_2O)_2]$ (**1c**), and $[Co^{III}Cl(tpp)]$ (**1d**) were prepared according to the literature methods.[1a,3,7]

$[Co^{III}Cl(oep)]$ (1b). $[Co^{II}(oep)]$ (1 mmol) was added to methanol (400 cm^3) containing conc. HCl (6 cm^3) and the mixture was vigorously stirred under air for 24 h. The solution was filtered to remove unchanged $[Co^{II}(oep)]$. Water (50—100 cm^3) was added to the filtrate and the mixture was condensed gradually under reduced pressure. The formed precipitate was collected, washed with water, and then dried under vacuum. Yield: 96%.

[1,2-Bis(methoxycarbonyl)etheno]-Co,C_{meso}-(2,3,7,8,12,13,17,18-octaethyl-5*H*,21*H*-porphyrinato)cobalt(III) Chloride (2b), Bromide (2b′), and Iodide (2b″). A mixture of $[Co^{III}X(oep)]$ [X=Cl (**1b**), Br (**1b′**), I (**1b″**)] (1 mmol) with DMAD (5 equiv) in 5 cm^3 of dry CH_2Cl_2, $CHCl_3$, or $C_2H_4Cl_2$ was stirred at temperature listed in Table 1. A solvent was removed and the residue was chromatographed quickly on silica gel with CH_2Cl_2–acetone (5:1). A brown elute was recrystallized from CH_2Cl_2–hexanes. (**2b**): ^1H NMR ($CDCl_3$) *meso*-H δ=6.39, 6.15 (s×2, 1H×2), 6.20 (s, 2H); OMe δ=3.80, 3.77 (s×2, 3H×2); CH_2 δ=ca. 2.3 (m, 16H); CH_3 δ=1.11, 1.09, 1.05, 0.98 (t×4, 6H×4). UV-vis (CH_2Cl_2) λ_{max} (log ε) 349 (4.33), 385 (sh), 477 (4.16) nm. Anal. Calcd for $C_{42}H_{50}N_4O_4ClCo\cdot(H_2O)$: C, 64.08; H, 6.66; N, 7.12%. Found: C, 64.39; H, 6.35; N, 6.86%. (**2b′**): ^1H NMR ($CDCl_3$) *meso*-H δ=6.44, 6.14 (s×2, 1H×2), 6.17 (s, 2H); OMe δ=3.79, 3.76 (s×2, 3H×2); CH_2 δ=ca. 2.3 (m, 16H); CH_3 δ=1.13, 1.10, 1.06, 0.99 (t×4, 6H×4). ^{13}C NMR ($CDCl_3$) CO δ=174.6, 159.9; pyrrole-$C_{\alpha,\beta}$ δ=152.5, 151.5, 149.7, 146.1, 145.1, 144.7, 144.2, 140.5; bridge-C 141.1; *meso*-C δ=121.9, 118.3, 45.8; OMe δ=52.4, 51.4; CH_2 δ=18.4, 17.7, 17.6, 17.5; CH_3 δ=16.7, 16.0, 15.8, 14.4. UV-vis (CH_2Cl_2) λ_{max} (log ε) 355 (4.37), 477 (4.25) nm. Anal. Calcd for $C_{42}H_{50}N_4O_4BrCo\cdot(H_2O)$: C, 60.65; H, 6.30; N, 6.74%. Found: C, 59.77; H, 5.91; N, 6.23%. (**2b″**): ^1H NMR ($CDCl_3$) *meso*-H δ=6.39, 6.15 (s×2, 1H×2), 6.20 (s, 2H); OMe δ=3.80, 3.77 (s×2, 3H×2); CH_2 δ=ca. 2.3 (m, 16H); CH_3 δ=1.11, 1.09, 1.05, 0.98 (t×4, 6H×4). UV-vis (CH_2Cl_2) λ_{max} 352, 380 (sh), 477 nm.

σ-(2-Chlorovinyl)Co(III) Porphyrin Complexes (3b, 3d, 4b, 4d, 5b, 6d). Alkyne (ca. 5 equiv) was added to dry CH_2Cl_2 solution (10 cm^3) of (**1b** or **1d**) and the solution was allowed to react under the conditions listed in Table 2. The solvent was removed and the residue was extracted with benzene. The benzene filtrate was evaporated and then recrystallized from CH_2Cl_2–methanol. If necessary, further purification was done by column chromatography on silica gel with CH_2Cl_2. Isolated yields were listed in Table 2. (**3b**): ^{13}C NMR ($CDCl_3$) CO δ=163.1; pyrrole-$C_{\alpha,\beta}$ δ=143.5, 143.9; *meso*-C δ=100.4; vinyl-C δ=98.6; OMe δ=49.3; CH_2 δ=20.0; CH_3 δ=18.4. UV-vis (CH_2Cl_2) λ_{max} 379, 514, 548 nm. IR (KBr) 1720 cm^{-1}. Anal. Calcd for $C_{40}H_{48}N_4O_2ClCo\cdot(H_2O)_{0.5}$: C, 66.70; H, 6.86; N, 7.78%. Found: C, 66.87; H, 6.65; N, 7.86%. (**3d**): UV-vis (CH_2Cl_2) λ_{max} 411, 523, 555 nm. Anal. Calcd for $C_{48}H_{32}N_4O_2CoCl$: C, 72.87; H, 4.08; N, 7.08%. Found: C, 72.92; H, 4.54; N, 6.80%. (**4b**): UV-vis (CH_2Cl_2) λ_{max} 390, 515, 550 nm. Anal. Calcd for $C_{38}H_{46}N_4ClCo\cdot(H_2O)_{0.5}$: C, 68.92; H, 7.15; N, 8.46%. Found: C, 68.77; H, 7.02; N, 8.37%. (**4d**): UV-vis (CH_2Cl_2) λ_{max} 409, 525, 555 nm. Anal. Calcd for $C_{46}H_{30}N_4ClCo$: C, 72.77; H, 3.98; N, 7.38%. Found: C, 73.09; H, 4.37; N, 7.36%. (**5b**): ^{13}C NMR ($CDCl_3$) pyrrole-$C_{\alpha,\beta}$ δ=143.1, 143.7; phenyl-C δ=139.4, 125.5, 123.5, 122.3; *meso*-C δ=99.9; vinyl-C δ=91.2; CH_2 δ=19.9; CH_3 δ=18.4. UV-vis (CH_2Cl_2) λ_{max} 391, 517, 551 nm. Anal. Calcd for $C_{44}H_{50}N_4ClCo\cdot(H_2O)$: C, 70.72; H, 7.01; N, 7.50%. Found: C, 70.92; H, 6.64; N, 7.84%. (**6d**): UV-vis (CH_2Cl_2) λ_{max} 411, 527, 555 nm. Anal. Calcd for $C_{47}H_{32}N_4OClCo$: C, 72.26; H, 4.39; N, 7.17%. Found: C, 71.74; H, 4.48; N, 6.97%.

σ-[2-(2,6-Dimethyl-1-pyridinio)vinyl]Co(III) Porphyrin Complexes (3a, 3c, 4a, 4c, 5a, 5c, 6a, 6c). Alkyne (ca. 5 equiv) was added to a mixture of (**1a** or **1c**) and 2,6-lutidine (5 equiv) in dry CH_2Cl_2. After the solution was stirred for 1 h at ambient temperature, the solvent was removed and the residue was chromatographed on silica gel with CH_2Cl_2–acetone (10:1). Recrystallization from CH_2Cl_2–hexanes afforded organocobalt(III) porphyrins in the yields listed in Table 2. (**3a**): ^{13}C NMR ($CDCl_3$) CO δ=162.8; lutidine-$C_{\alpha,\beta,\gamma}$ δ=154.2, 125.0, 144.0; pyrrole-$C_{\alpha,\beta}$ δ=143.2, 144.2; vinyl-C δ=115.8; *meso*-C δ=100.4; OMe δ=49.4; lutidine-CH_3 δ=18.6; CH_2 δ=19.8; CH_3 δ=18.4. UV-vis (CH_2Cl_2) λ_{max} 396, 552 nm. Anal. Calcd for $C_{47}H_{57}N_5O_6ClCo\cdot(H_2O)_2$: C, 61.47; H, 6.69; N, 7.62%. Found: C, 61.54; H, 6.42; N, 7.51%. (**3c**): UV-vis (CH_2Cl_2) λ_{max} 407, 524, 553 nm. Anal. Calcd for $C_{55}H_{41}N_5O_6ClCo\cdot(H_2O)_2$: C, 66.17; H, 4.54; N, 7.01%. Found: C, 65.93; H, 4.10; N, 7.57%. (**4a**): ^{13}C NMR ($CDCl_3$) lutidine-$C_{\alpha,\beta,\gamma}$ δ=153.1, 125.6, 143.6; pyrrole-$C_{\alpha,\beta}$ δ=143.6, 143.9; vinyl-C δ=118.0; *meso*-C δ=99.4; lutidine-CH_3 δ=19.4; CH_2 δ=19.8; CH_3 δ=18.4. UV-vis (CH_2Cl_2) λ_{max} 393, 517, 550 nm. Anal. Calcd for $C_{45}H_{55}N_5O_4ClCo\cdot(H_2O)$: C, 64.16; H, 6.82; N, 8.31%. Found: C, 63.85; H, 6.70; N, 8.36%. (**4c**): UV-vis (CH_2Cl_2) λ_{max} 433, 548 nm. Anal. Calcd for $C_{53}H_{39}N_5O_4ClCo$: C, 70.39; H, 4.35; N, 7.74%. Found: C, 69.95; H, 4.25; N, 7.48%. (**5a**); ^{13}C NMR ($CDCl_3$) lutidine-$C_{\alpha,\beta,\gamma}$ δ=152.8, 126.4, 144.4; pyrrole-$C_{\alpha,\beta}$ δ=142.9, 144.4; phenyl-C δ=133.6, 126.9, 126.8, 127.4; vinyl-C δ=128.5; *meso*-C δ=99.8; lutidine-CH_3 δ=20.0; CH_2 δ=19.8; CH_3 δ=18.3. UV-vis (CH_2Cl_2) λ_{max} 399, 554 nm. Anal. Calcd for $C_{51}H_{59}N_5O_4ClCo\cdot(H_2O)_{0.5}$: C, 67.35; H, 6.65; N, 7.70%. Found: C, 67.45; H, 6.74; N, 7.65%. (**5c**): UV-vis (CH_2Cl_2) λ_{max} 430, 540 nm. Anal. Calcd for $C_{59}H_{43}N_5O_4ClCo$: C, 72.28; H, 4.42; N, 7.14%. Found: C, 71.88; H, 4.29; N, 7.40%. (**6a, 6a′**): UV-vis (CH_2Cl_2) λ_{max} 396, 552 nm. Anal. Calcd for $C_{46}H_{57}N_5O_5ClCo\cdot(H_2O)_3$: C, 60.82; H, 6.99; N, 7.71%. Found: C, 61.08; H, 6.39; N, 7.63%. (**6c, 6c′**): UV-vis (CH_2Cl_2) λ_{max} 422, 540 nm. Anal. Calcd for $C_{54}H_{41}N_5O_5ClCo\cdot(H_2O)$: C, 66.84; H, 4.67; N, 7.22%. Found: C, 67.20; H, 4.13; N, 7.39%.

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