Reversible Complexation of Acetylene with (Perchlorato)cobalt(III) Porphyrins To Form a Novel Dicobalt(II) Bis(porphyrin) with a Vinylene-*N*,*N*′ Linkage

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(Perchlorato)cobalt(III) porphyrins bind acetylene reversibly in anhydrous CH_2Cl_2. The ^1H NMR and UV−vis spectra of the acetylene adduct at room temperature are characteristic of a Co^{II} N-substituted porphyrin. The ESR spectra of the acetylene adduct in CH_2Cl_2 at 4.2 and 77 K showed signals due to a π-cation radical and low-spin Co^{II}. These spectroscopic data show that one acetylene combines with two cobalt porphyrins to generate a vinylene-*N*,*N*′-linked bis(porphyrin) dicobalt(II) structure reversibly via an acetylene π-complex of Co^{II} porphyrin π-cation radical. When coordinating anionic axial ligands (Cl^-, SCN^-) were attached, the vinylene-*N*,*N*′ bis(tetraarylporphyrin) dicobalt(II) complexes were stabilized enough to be isolated and fully characterized.

Introduction

A number of organometallic porphyrin complexes have recently been synthesized, and their properties and reactivities have been studied with the aim of elucidating metabolic processes governed by heme and related metalloenzymes and also at developing new methodology for organic transformations.[1,2] Syntheses of carbene complexes,[3,4] π-complexes,[4−7] and σ-complexes[8] of metalloporphyrins have been reported so far. As far as metalloporphyrin π-complexes are concerned, only a few examples have been isolated or observed directly, and all of them are second- and third-row transition-metal π-complexes except for (η^5-cyclopentadienyl)Sc^{III}.[5] Collman's group prepared stable ethylene π-complexes of Ru^{II} and Os^{II} porphyrins,[4] and Weiss and co-workers reported a Mo^{II} alkyne π-complex.[6] Wayland and co-workers have shown ^1H NMR evidence indicating the formation of an ethylene π-complex of Rh^{III} through the acidification of (σ-β-hydroxyethyl)Rh^{III} porphyrin.[7] While a Co^{III} porphyrin π-complex with vinyl ether has been postulated as an intermediate leading to the formation of (σ-formylmethyl)Co^{III} porphyrin,[9] a π-complex of Co^{III} porphyrin has never been found thus far. We have recently shown that Co^{III} porphyrins react with alkynes in the presence of 2,6-lutidine, probably via a Co^{III} alkyne π-complex intermediate, to give (σ-vinyl)Co^{III} porphyrins with the 2,6-lutidine nitrogen bound at the β-vinylic carbon of the σ-vinyl moiety.[10] This reaction is mechanistically analogous to that of Co^{III} porphyrin with vinyl ether in the presence of ethanol. Thus, the present study is aimed at elucidating the basic reaction behavior of cationic Co^{III} porphyrins toward acetylene. Not only has the spectroscopic evidence indicating the reversible formation of a Co^{III} acetylene π-complex been obtained here but also novel vinylene-*N*,*N*′-linked bis(porphyrin) dicobalt(II) complexes have been isolated and characterized as the end products.

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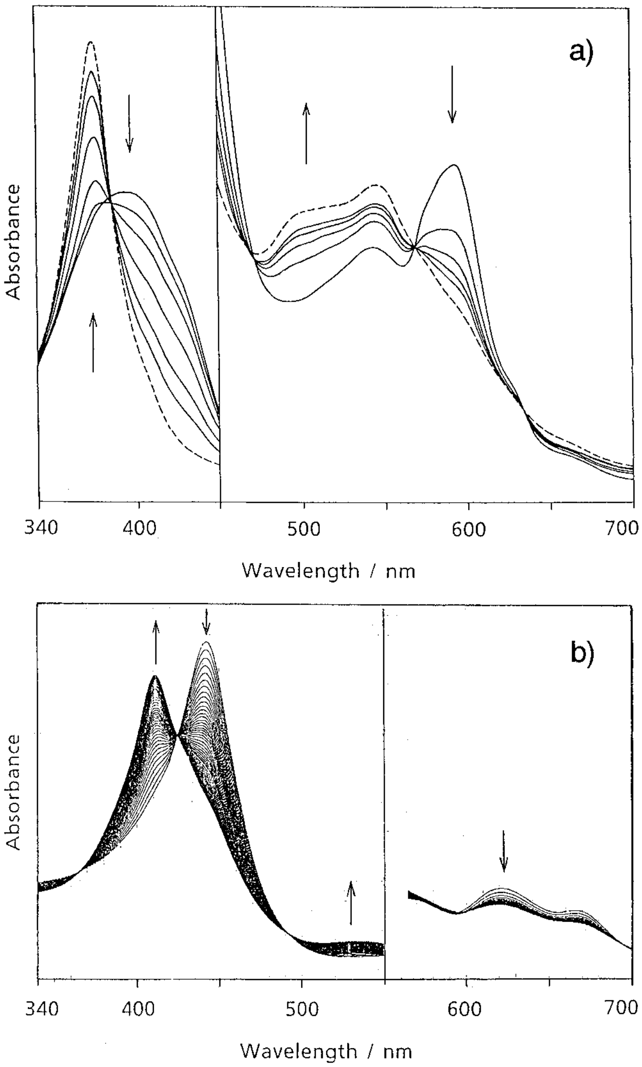

Figure 1. UV−vis spectral changes recorded at 1 min intervals after the dissolution of (a) the acetylene adduct C_2H_2−(**1a**) in CH_2Cl_2 (dotted line; after 30 min) and (b) the acetylene adduct C_2H_2−(**1b**).

Results and Discussion

Acetylene Adduct of $(OEP)Co^{III}(H_2O)_2ClO_4$ (1a). Introduction of purified acetylene gas into a CH_2Cl_2 solution of $(OEP)Co^{III}(H_2O)_2ClO_4$ (**1a**; OEP = octaethylporphyrin) caused an immediate color change from reddish brown to green. This color change is reversible. That is, rapid dissociation of acetylene to regenerate **1a** was observed by the UV−vis spectral change, giving four isosbestic points (387, 471, 570, and 633 nm) as shown in Figure 1a when the acetylene adduct C_2H_2−(**1a**), which was obtained by the precipitation with *n*-hexane, was dissolved in CH_2Cl_2 (Scheme 1). The ^1H NMR spectrum of a mixture of **1a** with excess acetylene in CD_2Cl_2 at 0 °C showed two 2H signals due to the meso protons at δ 11.6 and −9.0, the assignment of which was confirmed by using a *meso*-octaethylporphyrin-d_4 analogue. Eight 2H signals due to the peripheral CH_2 protons at 38.1, 30.9, 30.3, 28.1, 23.0, 20.3 (overlapped), and 19.3 ppm and four 6H signals due to the CH_3 protons at 10.2, 10.0, 9.5, and 3.9 ppm were also observed to indicate C_s symmetric molecular structure with a mirror plane containing a N(21)−Co−N(23) axis. Signals derived from acetylene could not be detected over the spectral range of ±200 ppm. As the temperature was lowered, these paramagnetic ^1H NMR signals broadened and an ESR signal became apparent as noted later.

The rhodo-type spectral pattern (398, 544, 592, and 629 nm) in the UV−vis and the molecular symmetry and the range of chemical shifts observed in the paramagnetic ^1H NMR spectrum of the adduct are consistent with a Co^{II} complex of N-substituted porphyrin. The similarity in the spectroscopic properties between the acetylene adduct and (*N*-(γ-IPr)OEP)$Co^{II}Cl$ (**2**)[11] is indicated in Table 1. It is remarkable that the Soret band of this acetylene adduct is blue-shifted by ca. 30 nm in comparison with ordinary N-substituted $(OEP)Co^{II}$ complexes. We had proposed in a preliminary communication that this acetylene adduct might be a d^6 high-spin Co^{III} complex with a vinylene-*Co,N* bridge.[12a] However, all the Co,N-bridged porphyrin complexes reported so far have a Co^{III} d^6 low-spin ($S = 0$) state,[13] and there seems to be no special demand for a high-spin state to be preferred in such a hypothetical etheno-*Co,N*-bridged Co^{III} complex.

It has been noted that the complex **1a** is a Co^{II} porphyrin π-cation radical and is ESR silent in dry CH_2Cl_2 solution in the temperature range 173−298 K, because the two unpaired electrons in the Co^{II} porphyrin π-cation radical structure are spin-coupled.[14] The acetylene adduct of **1a**, however, showed a strong ESR signal ($g = 2.002$; line width 14 G) in frozen CH_2Cl_2 (1 mM) at 77 K (see Figure 2a). This g value is indicative of a porphyrin π-cation radical. Whereas the intensity of this ESR signal was diminished to ca. 1% when the temperature was raised to 250 K, it was restored as the temperature was cooled down again to 77 K. The ESR spectrum of the acetylene adduct of **1a** at 4.2 K in a polycrystalline state showed the signals due to the unpaired electron at Co^{II} in addition to the signal due to the porphyrin π-cation radical (Figure 2b). Thus, the Co^{II} porphyrin π-cation radical structure was clearly evidenced by the ESR spectrum, since two spins do not interact with each other in this acetylene adduct, in contrast to the case for **1a**.

It was indicated that **1a** exists in dry CH_2Cl_2 as a form of Co^{II} porphyrin π-cation radical where a Co d_{z^2} orbital and a porphyrin π-orbital (a_{2u}) are singly occupied.[14] This was evidenced by the UV−vis spectrum (a blue-shifted Soret band and a broad and featureless Q-band) and the resonance Raman spectrum, both characteristic of porphyrin π-cation radicals. Addition of water or methanol gives rise to the normal Co^{III} porphyrin structure with two molecules of water (or MeOH) coordinating to the axial sites. The axial coordination of σ-donor ligands to Co would lift the energy of the d_{z^2} orbital to the extent enough to exceed the energy level of the porphyrin HOMO a_{2u} π-orbital, making a diradi-

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Scheme 1

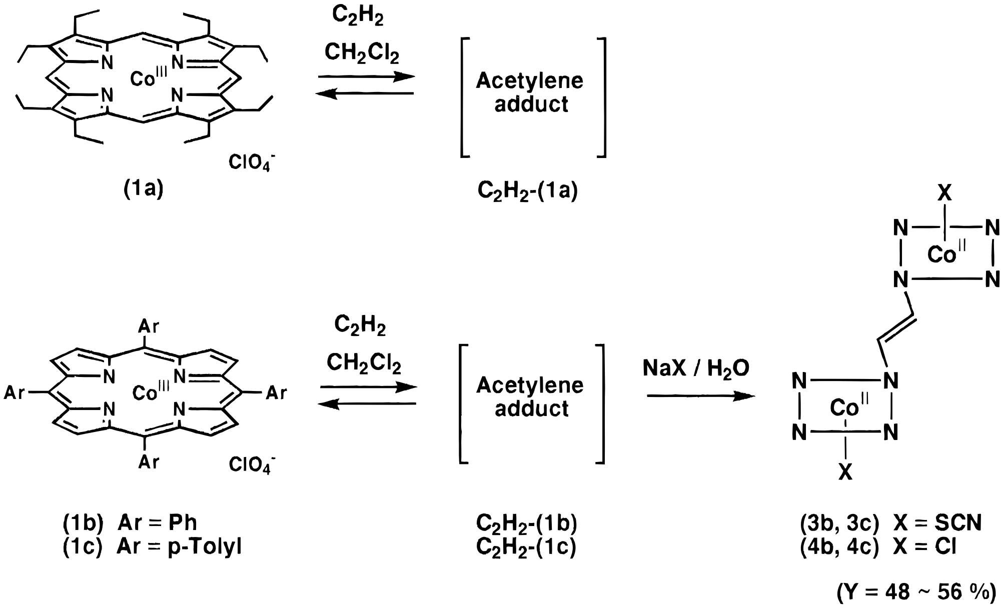

Table 1. ^{1}H NMR and UV–Vis Data for the Acetylene Adduct C_2H_2–(1a) of $(OEP)Co^{III}(H_2O)_2ClO_4$ (1a) and $(CH_2CH_2CH_2I$-*N*$)(OEP)Co^{II}Cl$ (2)

	^{1}H chem shifts (δ)[a]					λ_{max} (nm)[b]
	meso-H	–CH_2–		–CH_3	N–R	
C_2H_2–(**1a**)	11.6	38.1	23.0	10.2	n.d.	398
	−9.0	30.9	20.3	10.0		544
		30.3	20.3	9.5		592
		28.1	19.3	3.9		629
2	8.6	34.8	19.1	9.7	−117.5 (α)	428
	−5.9	26.3	18.4	6.5	−44.5 (β)	543
		24.1	16.5	5.8	−23.2 (γ)	584
		19.4	15.2	2.6		627

[a] Measured at 0 °C for C_2H_2–(**1a**) in CD_2Cl_2 and 23 °C for **2** in $CDCl_3$. [b] In CH_2Cl_2.

cal structure unfavorable. Coordination of acetylene to Co, however, would not change the Co^{II} porphyrin π-cation radical structure, probably because the energy level of the singly occupied d_{z^2} orbital is not raised, owing to the π-acceptor character of acetylene. Magnetic properties of various metalloporphyrin π-cation radicals have been interpreted in terms of the occupancy and symmetry of the orbitals on the metal and on the ligand that contain an unpaired electron.[15] It is not clear why coordination of acetylene disrupts the interaction between spins at Co^{II} and at the porphyrin π-system. Such a noninteracting two $S = 1/2$ spin system has been reported for Ru^{III} porphyrin π-cation radical, where ESR signals from the $S = 1/2$ ruthenium and $S = 1/2$ porphyrin π-cation radical are observed at 77 K.[16]

One of us previously studied the ESR spectra of a number of Co^{II} porphyrins with different axial ligations and found that there is a linear relationship between g values and hyperfine splittings (A).[17] The $g_\perp$–$A_\perp$ correlation has a positive slope, while the $g_\parallel$–$A_\parallel$ correlation has a negative slope. The $A_\perp$ value decreases from 400 G (in the case of four-coordinate complexes) to 100 G (in the case of five-coordinate complexes) and to −50 G (in the case of six-coordinate complexes) as the strength of the axial ligand field increases. Although ESR parameters for a parallel component have not been clearly determined in the present case (probably $g_\parallel = \sim 2$ and $A_\parallel = 160$ G), the values of a perpendicular component ($g_\perp = 3.1$; $A_\perp = 290$ G) conform well to this linear relationship and are in the range indicative of tetragonal Co^{II} coordination with a very weak axial ligand effect. This is consistent with the formation of an acetylene π-complex of a Co^{II} porphyrin π-cation radical.

Thus, the acetylene adduct of **1a** takes the form of a Co^{II} N-substituted porphyrin or the form of a Co^{II} porphyrin π-cation radical π-complexed with an axial acetylene, depending on temperature (Scheme 2).

Acetylene Adducts of $(TPP)Co^{III}(H_2O)_2ClO_4$ (1b) and $(TTP)Co^{III}(H_2O)_2ClO_4$ (1c). The adduct formation of $(TPP)Co^{III}(H_2O)_2ClO_4$ (**1b**) with acetylene occurred similarly to the case of **1a**. The reaction is also reversible, but the acetylene adduct, C_2H_2–(**1b**), went back much more slowly to **1b** than in the case of **1a** under the same reaction conditions. The UV–vis spectrum of the adduct is that of a rhodo-type characteristic of N-substituted porphyrin metal complexes showing absorption maxima at 443 (Soret), 568, 622, and 667 nm (see Table 2 and Figure 1b). While the ^{1}H NMR spectrum at room temperature did not show discrete signals, an ESR signal due to a π-cation radical was also observed in frozen CH_2Cl_2 (1 mM) at 77 K ($g = 1.99$; line width 35 G). When a saturated NaSCN or NaCl aqueous solution was added to a CH_2Cl_2 solution of the acetylene adduct, stable N-substituted Co^{II} porphyrins (**3b**) and (**4b**) were obtained in 48–56% yield after chromatographic purification on silica gel. The FAB MS spectrum of the TTP analogue **4c** showed a peak at the exact mass number (m/e 1553) corresponding to the molecular ion of a dimeric structure, (CH=CH-

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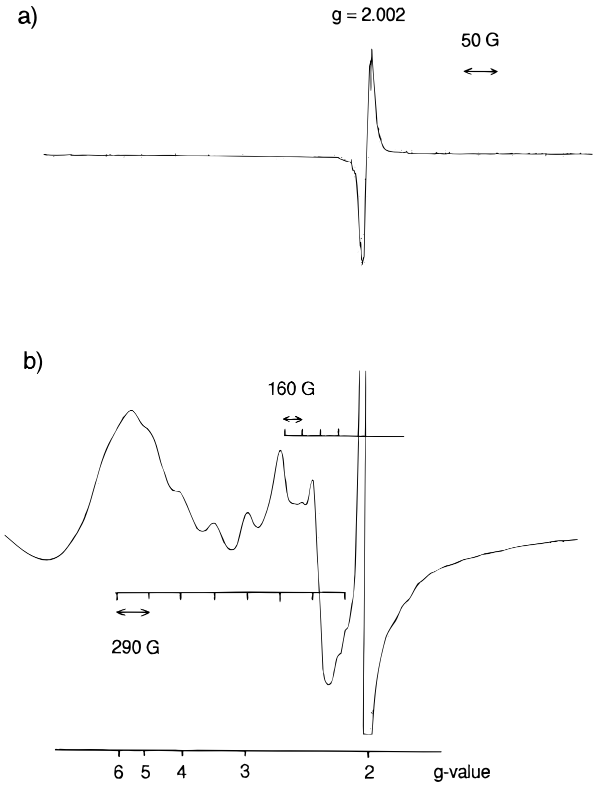
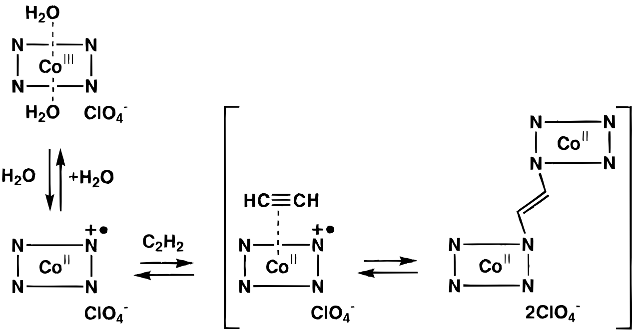


Figure 2. ESR spectra of (a) the acetylene adduct C_2H_2−(**1a**) in frozen CH_2Cl_2 at 77 K and (b) its polycrystalline sample at 4.2 K.

Scheme 2



N,*N*′)($TTPCo^{II}Cl)_2$. A similar treatment of the mixture of **1a** and acetylene with aqueous NaSCN or NaCl, however, resulted in the complete disappearance of the acetylene adduct to give a monomeric Co^{III} porphyrin. This means that the rates of the equilibrium for acetylene adduct formation and decomposition in the case of **1a** are fast enough to undergo exclusive axial ligation of water and halide to the monomeric Co^{III} porphyrin.

The complexes **3b** and **4b** retain the UV−vis spectral feature of the acetylene adduct which is virtually the same as that of (*N*-(*trans*-ClC(H)═CH)TPP)Co^{II}SCN (**5**),[18] as summarized in Table 2. The similarity in the ^{1}H NMR spectra of **3b** and **5** is also indicated in Table 2. A very sharp paramagnetic ^{1}H NMR spectrum was observed for **3b**, and the Curie plot (Figure 3) in the temperature range between 50 and −55 °C shows straight lines except for the highest field signal. This signal is assignable to the inside (region between the two porphyrin planes) ortho protons of the inner (region close to the *N*,*N*′ linkage) *meso*-aryl groups with respect to the center of the dimeric structure, and this deviation from a theoretical linear relationship should be attributed to the rotational barrier for a porphyrin nitrogen bond to a linking vinylene carbon, as will be discussed later. The signal assignment of **3b** was made in comparison with the spectra of a TPP-d_8 (deuteriated at the pyrrole β-positions) analogue (d_8-**3b**) and a TTP (tetra-*p*-tolylporphyrin) analogue (**3c**) and with the aid of line-width analysis (Figure 4) and a ^{1}H−^{1}H COSY spectrum (Figure 5).[19] Of special interest is the 2H absorption at −178 ppm due to the vinylene-*N*,*N*′ protons. This chemical shift is quite close to the summation of the chemical shifts of the α- (−69.6 ppm) and the β-vinyl (−95.1 ppm) protons of the *N*-*trans*-β-chlorovinyl moiety of **5**.[18] This means that the vinylene-*N*,*N*′ proton of **3b** is subject to isotropic shifts from the two chemically equivalent but magnetically nonequivalent Co^{II} atoms of the *trans*-vinylene-*N*,*N*′-linked bis(porphyrin) structure. This chemical shift is not consistent with a *cis*-vinylene-*N*,*N*′-linked bis(porphyrin) structure, since a geometric factor is quite important in the isotropic shifts for protons in the proximity of a paramagnetic center. The analysis of the diamagnetic ^{1}H NMR spectrum of the corresponding free base **6b**, which was readily obtained by the demetalation of **3b** with trifluoroacetic acid, is also consistent with the *trans*-vinylene-*N*,*N*′-linked dimeric structure. A 2H proton singlet at −5.32 ppm is associated with the vinylene-*N*,*N*′ protons, and a rough estimation of the ring current term for this signal (Δδ = ca. −10 ppm, taking a reference chemical shift as δ 5 for vinylic

Table 2. ^{1}H NMR and UV−Vis Data for the Acetylene Adduct C_2H_2−(1b) of (TPP)$Co^{III}(H_2O)_2ClO_4$ (1b), (CH═CH-*N*,*N*′)($TPPCo^{II}SCN)_2$ (3b), and (CH═CHCl-*N*)($TPPCo^{II}$SCN) (5) and Their Free Bases 6b and 7

	^{1}H chem shifts (δ)[a]					
	py β-H	*o*-H	*m*-H	*p*-H	N−R	λ_{max} (nm)[b]
C_2H_2−(**1b**)			n.d.			443
						568
						622
						667
3b	41.8	20.8	15.4	8.7	−178[c]	442
	40.2	16.3	13.9	9.9		567
	33.8	9.5	11.8			618
	−3.4	−0.6	5.8			661
6b	8.86		8.5−5.4		−5.32[c]	415
	8.27					531
	7.96					571
	6.12					623
						683
5	44.2	23.3	13.5	9.5	−69.6[c]	447
	44.2	19.6	12.2	7.6	−95.1[d]	569
	35.9	2.5	7.3			618
	−1.9	−3.0	7.1			667
7	8.99		8.4−7.6		2.30[d]	433
	8.91				−1.45[c]	529
	8.61					569
	8.46					617
						672

[a] Measured at room temperature in $CDCl_3$. [b] In CH_2Cl_2. [c] NCH═. [d] NC═CHCl.

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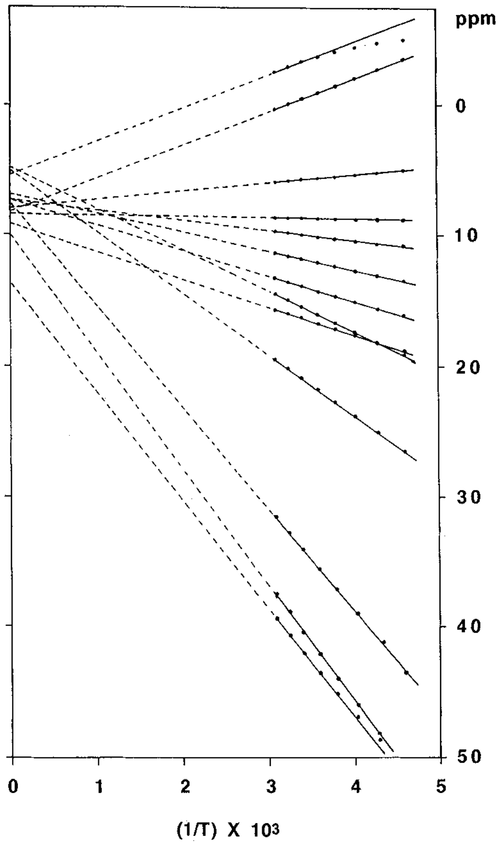

Figure 3. Curie plots of paramagnetic chemical shifts in $\mathrm{CDCl_3}$ against temperature (15 °C intervals between 50 and −55 °C) for the signals of (CH=CH-*N*,*N*′)(TPPCo$^{\mathrm{II}}$-SCN)$_2$ (**3b**).

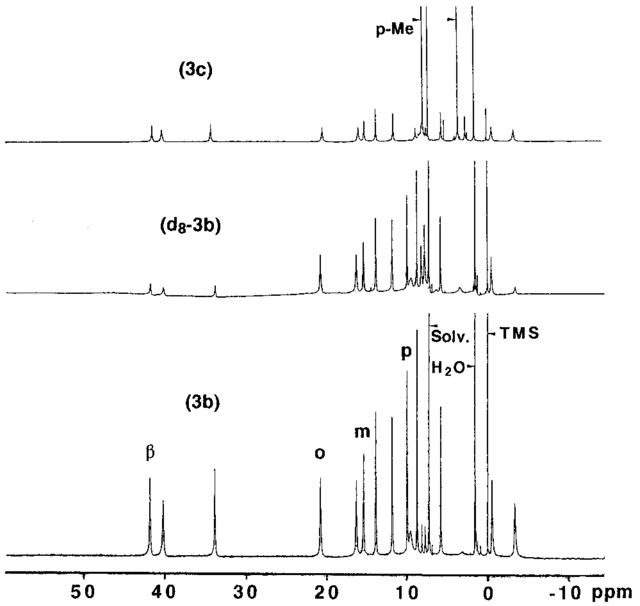

Figure 4. ^{1}H NMR spectra of (CH=CH-*N*,*N*′)(TPPCo$^{\mathrm{II}}$-SCN)$_2$ (**3b**) (bottom), *d*$_8$-**3b** (middle), and (CH=CH-*N*,*N*′)-(TTPCo$^{\mathrm{II}}$SCN)$_2$ (**3c**) (top) at room temperature.

protons) is in good accordance with the summation of the ring current terms at the α-vinylic proton ($\Delta\delta$ = ca. −6.5 ppm) and the β-vinylic proton ($\Delta\delta$ = ca. −2.7 ppm) of the *N*-*trans*-β-chlorovinyl moiety of the free base **7** derived from **5**, which were observed at δ −1.45 and 2.30, respectively (see Table 2). The unusually upfield shifted signals due to the β-pyrrole protons at 6.06 ppm and the *meso*-phenyl ortho protons at 5.51 ppm imply

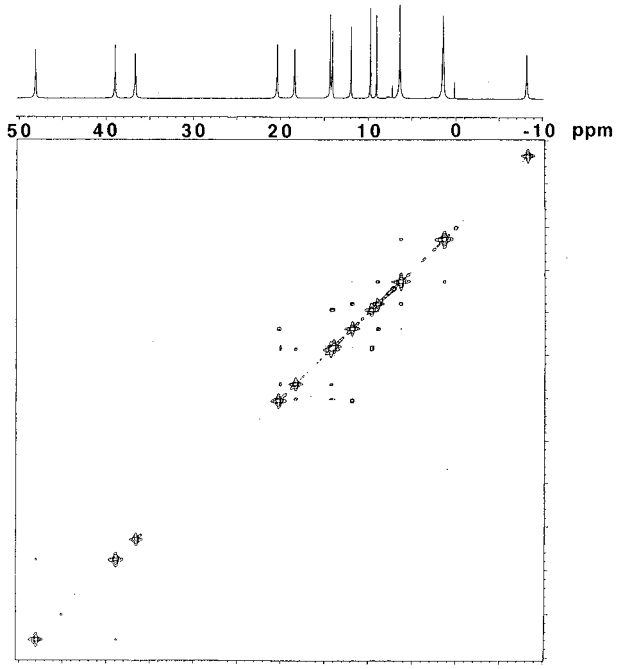

Figure 5. ^{1}H−^{1}H COSY spectrum of (CH=CH-*N*,*N*′)-(TPPCo$^{\mathrm{II}}$Cl)$_2$ (**4b**) in $\mathrm{CDCl_3}$ at room temperature.

that these protons are in the shielding regions of the other half-porphyrin moiety of the dimeric structure. The FAB MS ion peak at *m*/*e* 1367 ((M + H)$^+$) provided evidence in support of the dimeric structure of the TTP analogue, (CH=CH-*N*,*N*′)(TTPH)$_2$ (**6c**).

Therefore, **3b** should have *trans*-vinylene-*N*,*N*′-linked bis(porphyrin) dicobalt(II) structure. Since the spectroscopic properties of the acetylene adducts derived from **1a** and **1b** at room temperature are best rationalized in terms of the N-substituted Co$^{\mathrm{II}}$ porphyrin, the reversibility between the formal trivalent complex **1** and its divalent acetylene adduct complex without apparent redox counterparts necessitates a dimeric structure for these acetylene adducts. It is remarkable that the vinylene-*N*,*N*′-linked bis(tetraarylporphyrin) dicobalt(II) structure is stabilized by the axial coordination of chloride and thiocyanate. The axial ligand coordination causes deviation of Co atom out of the porphyrin plane toward axial ligands,[20] and this would weaken the interaction between cobalt and the vinylene-*N*,*N*′ moiety, which leads to the scission of the N−C bond. In fact, treatment of **3c** with $\mathrm{AgClO_4}$ in $\mathrm{CH_2Cl_2}$ resulted in the complete degradation of the dimeric structure, probably by way of replacement of chloride in the axial coordination site by perchlorate (Scheme 3).

A number of the layered bis(porphyrin) structures have recently been prepared for the purpose of creating molecular systems effective for electron transfer and bimetallic catalysis.[21−23] They include bis(porphyrins) linked through the peripheral substituents,[21] axial ligation,[22] and metal elements.[23] While the coordination

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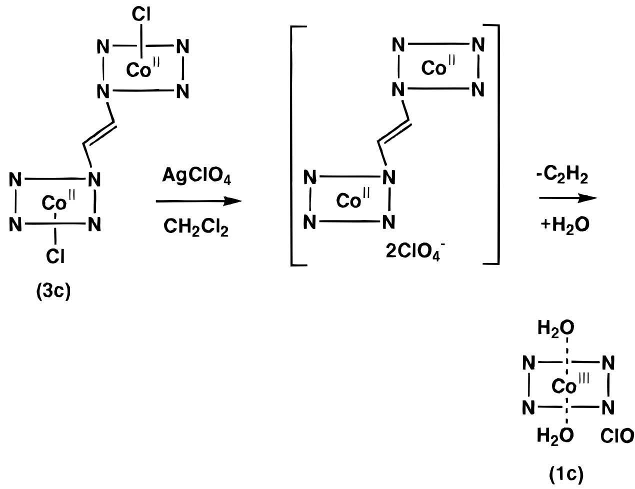
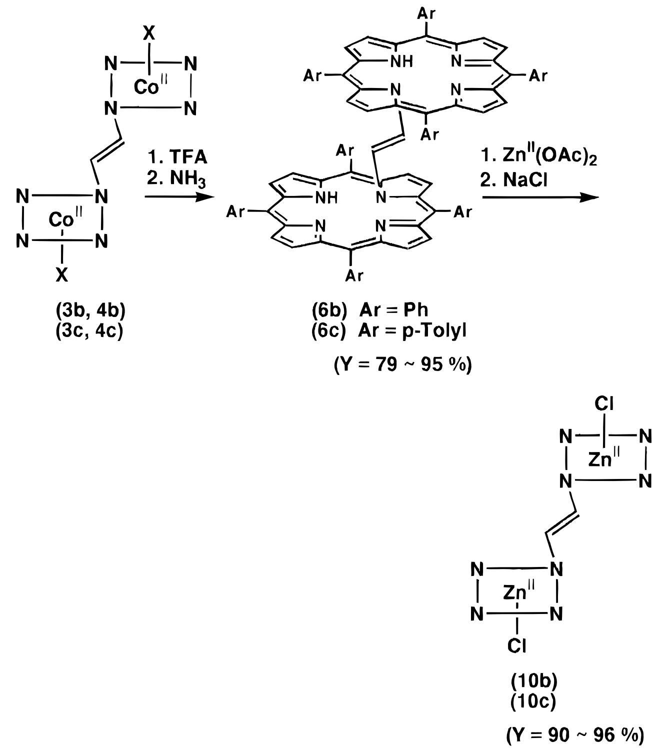
Scheme 3



of porphyrin *N*-oxide to a metalloporphyrin has been reported to provide a bis(porphyrin) system joined with a M−O−N link as the first bis(porphyrin) system utilizing N-substituted porphyrins,[24] the present vinylene-*N*,*N*′-linked bis(porphyrin) system is of wide application because its covalently bound unique dimeric structure allows one to make various homo- and heterobimetallic complexes (Scheme 4).

Mechanism of the Dimer Formation. We have already reported that an electrophilic Co^{III} and a nucleophilic nitrogen base add across a C−C triple bond of methyl propiolate to give organocobalt(III) complexes.[10] That is, intermolecular attack of a 2,6-lutidine nitrogen gives a (σ-vinyl)Co^{III} complex, (Por)Co^{III}(C(CO$_2$Me)=CHN(C$_7$H$_9$))ClO$_4$ (**8**), while intramolecular attack of a porphyrin nitrogen affords the etheno-*C*,*N*-bridged Co^{III} complex (C(CO$_2$Me)=CH-*Co*,*N*)(Por)Co^{III}ClO$_4$ (**9**) (Scheme 5). These reactions suggest that an acetylene-π-coordinated cobalt intermediate, (π-C$_2$H$_2$)Co^{II}(Por$^{\bullet+}$)-ClO$_4$, undergoes σ-π rearrangement to generate a (σ-vinyl)Co^{III} structure (**A**) in which a β-carbon atom with respect to Co^{III} is cationic (see Scheme 6). Therefore, an etheno-*Co*,*N*-bridged Co^{III} intermediate (**B**) would be formed and it should undergo homolytic cleavage of a Co^{III}−C σ-bond to provide a vinyl radical species (**C**) attached at the nitrogen of the cobalt porphyrin. As it is well-known that the rate of the Co^{III}−C bond-forming reaction between low-spin Co^{II} complexes and alkyl radicals is generally on the order of diffusion control,[25] this vinyl radical (**C**) would be immediately captured by complex **1**, since it takes a Co^{II} π-cation radical structure. Thus, the generated bis(porphyrin) with (σ-vinyl)Co^{III} porphyrin π-cation radical structure (**D**) would automatically undergo Co-to-N migration of the σ-vinyl group to provide vinylene-*N*,*N*′-linked bis(porphyrin) dicobalt(II) complexes. A (σ-alkyl)Co^{III} porphyrin π-cation radical has long been thought to be a key intermediate in the reversible Co-to-N migration of a σ-alkyl group upon one-electron oxidation of (σ-alkyl)-Co^{III} porphyrins.[1,26] A recent study has indicated that the migration of an alkyl and an aryl group from Co to nitrogen will only occur after the initial formation of a transient σ-bonded Co^{IV} derivative rather than a σ-bonded Co^{III} porphyrin π-cation radical, on the basis of the ESR evidence.[27] That is, the isotropic *g* values (~2.02) observed at 77 K for the one-electron-oxidized intermediates from (σ-alkyl)Co^{III} porphyrins are reported to agree well with those for organocobalt(IV) species.[28] Thus, the bis(porphyrin) intermediate with a (σ-vinyl)-Co^{III} porphyrin π-cation radical structure (**D**) in the present case might better be described as a form of (σ-vinyl)Co^{IV} structure, (Por)Co^{IV}−CH=CHN(Por)Co^{II}(ClO$_4$)$_2$ (**D′**).

Scheme 4



Since the ESR *g* value (2.002) observed at 77 K for the acetylene adduct C$_2$H$_2$−(**1a**) is not consistent with the Co^{IV} structure as noted above, the observed ESR signal is not associated with the structure **D′**. We

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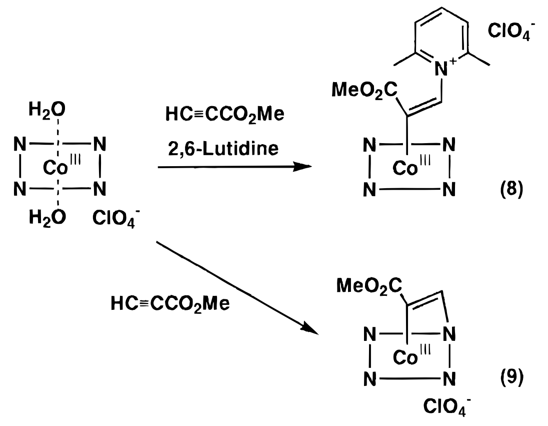
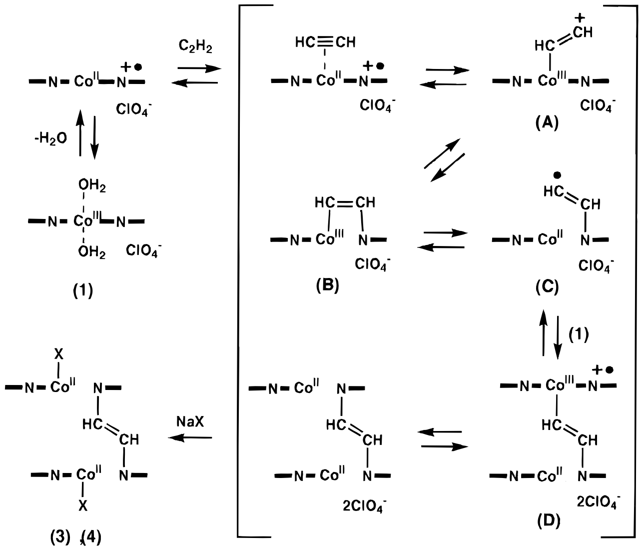
Scheme 5



Scheme 6



consider the acetylene π-complex intermediate (π-C_2H_2)-$Co^{II}(Por^{\bullet+})ClO_4$ to be responsible for the ESR signal. Furthermore, the ESR parameters due to Co^{II} of the acetylene adduct are those of a low-spin ($S = {}^1/_2$) type[17] and are not consistent with those for Co^{II} N-substituted porphyrins, which generally show a high-spin ($S = {}^3/_2$) type ESR ($g_\perp = 4.4$, $g_\parallel = 2.04$ for (*N*-MeOEP)-$Co^{II}(OAc)$).[29] Therefore, the ESR spectra of the acetylene adduct are not explainable in terms of the hypothetical bis(porphyrin) intermediate **D** or **D′**, which must have an $S = {}^3/_2$ spin at the Co^{II} site even if a noninteracting two-spin system might be possible in such a bis(porphyrin) framework.

It is remarkable that acetylene is reversibly complexed with cobalt porphyrin as a vinylene-*N*,*N′* linkage and that an acetylene-π-complexed Co^{II} porphyrin π-cation radical structure and a vinylene-*N*,*N′* bis(porphyrin) dicobalt(II) structure are thermally equilibrated, as evidenced by the ESR and NMR spectroscopy.

Dynamic Behavior. Figure 6 shows temperature-dependent ^1H NMR spectra of the aromatic regions of **6c** and its dizinc complex (**10c**). The aromatic region of the dizinc complex shows two sets of four doublets associated with the outer *meso*-tolyl groups (δ 7.95−7.5) and the inner *meso*-tolyl groups (δ 7.35−5.1). The extremely upfield shifted doublet at δ 5.10 is assigned to the inside (region between the two porphyrin planes) ortho protons of the inner (region close to the *N*,*N′* linkage) *meso*-aryl groups, because these protons are located in the strongly shielding region due to the porphyrin ring current effect from the other half-moiety. The signal broadening of all the aromatic protons of **10c** takes place simultaneously with increasing temperature, and this is explained in terms of the hindered rotation of the *meso*-aryl groups (Figure 6; right side). The coalescence temperature is similar to that observed for an N-methylated tetraarylporphyrin reported recently.[30] The aromatic protons due to the outer *meso*-tolyl groups of the free base **6c** appear as a set of four doublets between 8.7 and 7.4 ppm (Figure 6; left side). Comparison of the temperature-dependent line-broadening behavior of these signals with that of **10c** indicates that the rotation of *meso*-tolyl groups of the free base is more hindered than that of the zinc complex. Whereas the four doublets due to the outer *meso*-tolyl groups of **6c** are broadened uniformly with increasing temperature, signals due to the inner *meso*-tolyl groups (δ 7.3−5.1) showed unusual dynamic behavior with the same temperature change. While the signal due to the inside ortho proton at δ 5.10 is extremely broadened at 25 °C, the other aromatic protons appear as sharp signals at ~7.2 ppm at this temperature. Therefore, the specific broadening of the ortho proton signal at 5.10 ppm would be ascribable to the restricted rotation around the bond between the porphyrin nitrogen and the linking vinylene carbon but not to the hindered rotation of the tolyl groups. The above observation shows that the dynamic molecular motion of the vinylene-*N*,*N′*-linked bis(porphyrins) is greatly influenced by the metalation, which changes and fixes the shape of porphyrin planes.

Conclusion

We have delineated a novel reaction behavior of cationic Co^{III} porphyrins with acetylene. Spectroscopic measurements showed that acetylene is reversibly complexed with (perchlorato)Co^{III} porphyrin in dry CH_2Cl_2 solution. This acetylene adduct underwent a reversible structural change depending on temperature between (π-C_2H_2)$Co^{II}(Por^{\bullet+})ClO_4$ at low temperature and Co^{II}-(Por)(CH=CH-*N*,*N′*)(Por)$Co^{II}(ClO_4)_2$ at room temperature. The presence of two noninteracting $S = {}^1/_2$ spins at Co and at the porphyrin π-system was evidenced by the ESR signals at 4.2 K, while a paramagnetic NMR spectrum characteristic of Co^{II} complexes of N-substituted porphyrins was observed at room temperature. The vinylene-*N*,*N′*-linked bis(porphyrin) dicobalt(II) complexes have been isolated in moderate yields by the addition of an axially coordinating ligand such as a chloride ion. The free base bis(porphyrins) with a vinylene-*N*,*N′* linkage obtained here by a convenient procedure are of wide application because their covalently bound dimeric structure allows easy access to a novel face-to-face bis- and poly(porphyrin) metal complexes. An extensive study in this regard is under way in our laboratory.

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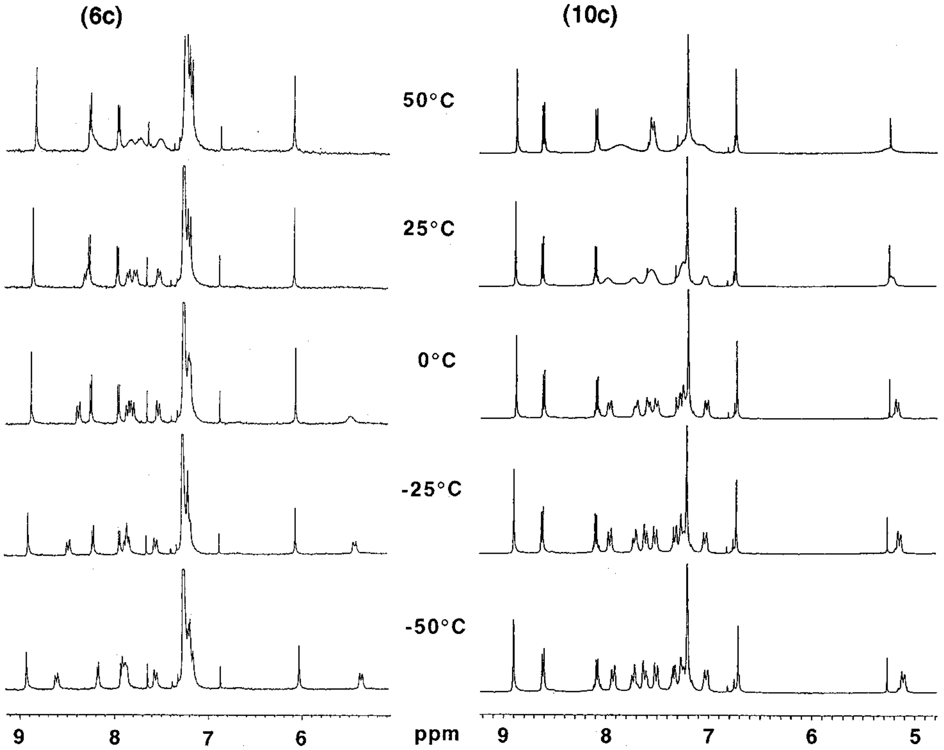

Figure 6. Variable-temperature ^1H NMR spectra in the aromatic region of (CH=CH-*N*,*N*′)(TTPH)$_2$ (**6c**) (left) and (CH=CH-*N*,*N*′)(TTPZn^{II}Cl)$_2$ (**10c**) (right) in $CDCl_3$.

Experimental Section

Dichloromethane was dried by distilling from calcium hydride and stored over 4A molecular sieves. Extra-pure acetylene gas (99.99%) was courteously supplied by Nichigo Acetylene Co. Ltd. Osaka, Japan. (TPP)H_2, (TTP)H_2, and (OEP)H_2 and their deuteriated analogues were prepared according to the literature.[31,32] (Perchlorato)cobalt(III) porphyrins were prepared according to the literature.[9,14]

^1H NMR spectra were measured on JEOL GX-270 (270 MHz) and Bruker AC-250 (250 MHz) spectrometers, and the chemical shifts are referenced to tetramethylsilane as an internal standard. A JEOL FE-3X X-band spectrometer equipped with an Air Product Model LTR-3-110 Heli-Tran liquid-helium-transferring refrigerator was used for ESR measurement at liquid-helium temperature. FAB MS spectra were obtained at the acceleration voltage of 8 kV (Xe, 7 kV) using *m*-nitrobenzyl alcohol as a matrix on a Shimadzu/Kratos CONCEPT IS mass spectrometer.

Vinylene-*N*,*N*′ Bis(porphyrin) Dicobalt(II) Complexes (3b,c and 4b,c). Purified acetylene gas was introduced into a flask containing (tetraarylporphyrinato)cobalt(III) perchlorate **1b** or **1c** (150 mg; 0.186 mmol for **1b** or 0.174 mmol for **1c**) in dry CH_2Cl_2 (50 mL) with stirring at room temperature. The color of the solution changed rapidly to bright green. After the mixture was stirred for 15 min, saturated NaSCN or NaCl aqueous solution (50 mL) was added at once with vigorous stirring. The organic layer was separated, washed with water, and dried over anhydrous Na_2SO_4. It was then condensed with a rotary evaporator and chromatographed on silica gel (Wakogel C-300, Wako Junyaku). The first green band eluted with CH_2Cl_2 was evaporated to dryness, and the residue was recrystallized from CH_2Cl_2−methanol to give (CH=CH-*N*,*N*′)(TPPCo^{II}SCN)$_2$ (**3b**) and (CH=CH-*N*,*N*′)(TTPCo^{II}SCN)$_2$ (**3c**) in yields of 48−56%. (CH=CH-*N*,*N*′)(TPPCo^{II}Cl)$_2$ (**4b**) and (CH=CH-*N*,*N*′)(TTPCo^{II}Cl)$_2$ (**4c**) were obtained similarly after purification by silica gel chromatography with CH_2Cl_2−acetone (10:1) and recrystallization from CH_2Cl_2−methanol or CH_2Cl_2−diethyl ether. **3b**: ^1H NMR (δ, in $CDCl_3$) 41.8, 40.2, 33.8, −3.4 (4H × 4, pyrrole β-H), 20.8, 16.3, 9.5, −0.6 (4H × 4, Ph *o*-H), 15.4, 13.9, 11.8, 5.8 (4H × 4, Ph *m*-H), 9.5, 8.7 (4H × 2, Ph *p*-H); UV−vis (λ_{max} (log ε) in CH_2Cl_2) 442 (5.33), 567 (4.07), 618 (4.22), 661 (4.00) nm. Anal. Calcd for $C_{92}H_{58}N_{10}S_2Co_2{\cdot}H_2O$: C, 73.49; H, 4.02; N, 9.32. Found: C, 73.55; H, 3.52; N, 9.22. **3c**: ^1H NMR (δ, in $CDCl_3$) 41.5, 40.3, 34.3, −3.3 (4H × 4, pyrrole β-H), 20.4, 15.9, 8.8, −0.6 (4H × 4, Ar *o*-H), 15.2, 13.7, 11.6, 5.6 (4H × 4, Ar *m*-H), 7.9, 3.6 (12H × 2, Ar *p*-Me); UV−vis (λ_{max} (log ε) in CH_2Cl_2) 445 (5.29), 570 (4.06), 621 (4.21), 666 (4.03) nm. Anal. Calcd for $C_{100}H_{74}N_{10}S_2Co_2{\cdot}H_2O$: C, 74.09; H, 4.74; N, 8.67. Found: C, 74.09; H, 4.40; N, 8.60. **4b**: ^1H NMR (δ, in $CDCl_3$) 48.6, 39.4, 37.0, −8.5 (4H × 4, pyrrole β-H), 20.5, 18.5, ~6.3, 1.2 (4H × 4, Ph *o*-H), 14.4, 14.1, 11.9, 6.3 (4H × 4, Ph *m*-H), 9.7, 9.0 (4H × 2, Ph *p*-H); UV−vis (λ_{max} (log ε) in CH_2Cl_2) 445 (5.22), 569 (3.95), 617 (4.12), 663 (3.94) nm. Anal. Calcd for $C_{90}H_{58}N_8Cl_2Co_2{\cdot}C_4H_{10}O$: C, 74.55; H, 4.53; N, 7.40. Found: C, 74.43; H, 4.62; N, 7.41. **4c**: ^1H NMR (δ, in $CDCl_3$) 48.1, 39.5, 36.8, −8.4 (4H × 4, pyrrole β-H); 20.1, 18.1, 5.4, 1.1 (4H × 4, Ar *o*-H), 14.3, 14.0, 11.7, 6.1 (4H × 4, Ar *m*-H), 7.7, 3.8 (12H × 2, Ar *p*-Me), −178 (2H, NCH=CHN). FAB MS *m*/*e* 1553 ((M + H)$^+$), 1454 ((TTPCo)$_2^+$), 727 ((TTPCo)$^+$); UV−vis (λ_{max} (log ε) in CH_2Cl_2) 447 (5.27), 575 (4.06), 618 (4.13), 665 (3.95) nm. Anal. Calcd for $C_{98}H_{74}N_8Cl_2Co_2$: C, 74.10; H, 4.95; N, 7.05. Found: C, 73.97; H, 4.50; N, 7.03.

Vinylene-*N*,*N*′ Bis(porphyrin) Free Bases (6b,c). Trifluoroacetic acid (4 mL) was added to a dry CH_2Cl_2 solution (50 mL) of (CH=CH-*N*,*N*′)(TPPCo^{II}SCN)$_2$ (**3b**) or (CH=CH-*N*,*N*′)(TTPCo^{II}SCN)$_2$ (**3c**) (150 mg; 0.101 mmol for **3b** or 0.094 mmol for **3c**), and the mixture was stirred for 15 min at room temperature. Aqueous ammonia (28%) sufficient to neutralize CF_3COOH was added cautiously until the green solution turned brown. Fine crystals formed in the organic layer were filtered, washed with water, and dried under vacuum. The organic layer was separated, dried over Na_2SO_4, and condensed. Hexane was added to this residue to afford precipitates. The combined precipitates were recrystallized from CH_2Cl_2−hexane to afford (CH=CH-*N*,*N*′)(TPPH)$_2$ (**6b**) and

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(CH=CH-*N*,*N*′)$(TTPH)_2$ (**6c**) in 79−95% yields. **6b**: ^{1}H NMR (δ, in $CDCl_3$) 8.86, 6.12 (s × 2, 4H × 2, pyrrole β-H), 8.27, 7.96 (d × 2, 4H × 2, pyrrole β-H), 8.5−5.4 (m, 40H, Ph H), −3.1 (bs, 2H, NH), −5.32 (s, 2H, bridge NCH=); UV−vis (λ_{max} (log ϵ) in CH_2Cl_2) 415 (5.39), 531 (4.15), 571 (4.17), 623 (3.80), 683 (3.82) nm. Anal. Calcd for $C_{90}H_{60}N_8 \cdot CH_2Cl_2$: C, 81.66; H, 4.67; N, 8.37. Found: C, 81.60; H, 4.39; N, 8.05. **6c**: ^{1}H NMR (δ, in $CDCl_3$) 8.86, 6.08 (s × 2, 4H × 2, pyrrole β-H); 8.26, 7.96 (d × 2, 4H × 2, pyrrole β-H); 8.3−5.4 (m, 32H, Ar H), 2.79, 2.57 (s × 2, 12H × 2, Ar *p*-Me), −3.1 (bs, 2H, NH), −5.33 (s, 2H, bridge NCH=); FAB MS *m*/*e* 1367 ($(M + H)^+$), 695 ($(M - (TTP)H_2)^+$), 683, 670 ($(TTPH)^+$); UV−vis (λ_{max} (log ϵ) in CH_2Cl_2) 425 (5.52), 532 (4.04), 576 (4.26), 625 (4.10), 680 (4.10) nm. Anal. Calcd for $C_{98}H_{76}N_8 \cdot CH_2Cl_2$: C, 81.96; H, 5.42; N, 7.72. Found: C, 82.58; H, 5.20; N, 7.73.

***N*,*N*′−Vinylene Bis(porphyrin) Dizinc(II) Complexes (10b,c).** To the free base **6b** or **6c** (50 mg; 0.037 mmol for **6b** or 0.034 mmol for **6c**) dissolved in CH_2Cl_2 (30 mL) was added a saturated MeOH solution (5 mL) of $Zn^{II}(OAc)_2 \cdot 2H_2O$. After a slight excess amount of 2,6-lutidine was added, the green solution was stirred at room temperature for 1 h. The resulting solution was evaporated to dryness, and the residue was extracted with CH_2Cl_2. The CH_2Cl_2 solution was vigorously shaken with saturated NaCl aqueous solution for 1 h, dried over Na_2SO_4, and then evaporated to dryness. The green residue was chromatographed on silica gel with CH_2Cl_2−acetone (10:1) to give (CH=CH-*N*,*N*′)$(TPPZn^{II}Cl)_2$ (**10b**) and (CH=CH-*N*,*N*′)$(TTPZn^{II}Cl)_2$ (**10c**) in 90−96% yield. **10b**: ^{1}H NMR (δ, in $CDCl_3$) 8.92, 6.84 (s × 2, 4H × 2, pyrrole β-H), 8.66, 8.15 (d × 2, 4H × 2, pyrrole β-H), 7.9−5.4 (m, 40H, Ar H), −5.86 (s, 2H, bridge NCH=); FAB MS *m*/*e* 1452 ($(M)^+$), 1417 ($(M - Cl)^+$), 676 ($(TPPZn)^+$); UV−vis (λ_{max} (log ϵ) in CH_2Cl_2) 437 (5.90), 566 (4.24), 613 (4.48), 663 (4.22) nm. Anal. Calcd for $C_{90}H_{58}N_8Cl_2Zn_2 \cdot H_2O$: C, 73.48; H, 4.11; N, 7.62. Found: C, 73.45; H, 4.59; N, 7.43. **10c**: ^{1}H NMR (δ, in $CDCl_3$) 8.92, 6.78 (s × 2, 4H × 2, pyrrole β-H), 8.66, 8.16 (d × 2, 4H × 2, pyrrole β-H), 8.0−5.2 (m, 32H, Ar H), 2.78, 2.60 (s × 2, 12H × 2, Ar *p*-Me), −5.86 (s, 2H, bridge NCH=); UV−vis (λ_{max} (log ϵ) in CH_2Cl_2) 438 (5.65), 565 (4.12), 615 (4.35), 664 (4.21) nm. Anal. Calcd for $C_{98}H_{74}N_8Cl_2Zn_2$: C, 75.19; H, 4.76; N, 7.16. Found: C, 74.10; H, 4.78; N, 6.80.

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