Synthesis of N21,N22-etheno-bridged porphyrins by the reactions of cobalt porphyrins with alkynes in the presence of iron(III) salts

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Organometallics, **1991**, 10 (4), 1099-1107• DOI: 10.1021/om00050a048 • Publication Date (Web): 01 May 2002

Organometallics is published by the American Chemical Society. 1155 Sixteenth Street N.W., Washington, DC 20036

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Synthesis of N^{21},N^{22}-Etheno-Bridged Porphyrins by the Reactions of Cobalt Porphyrins with Alkynes in the Presence of Iron(III) Salts

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Received June 28, 1990

Novel organocobalt(III) porphyrins with an alkyne inserted into an N–Co bond of diaquo(porphyrinato)cobalt(III) perchlorates could be isolated by using dimethyl acetylenedicarboxylate and methyl propiolate. These complexes were converted into N^{21},N^{22}-etheno-bridged porphyrins through the oxidative cobalt-to-nitrogen shift of the vinylic carbon when treated with excess $FeCl_3$. Cobalt(III) porphyrin π cation radicals with a weakly coordinating axial ligand reacted smoothly with diphenylacetylene directly to afford the N^{21},N^{22}-etheno-bridged porphyrin in good yields. Vacancy in the axial coordination site of the Co(III) porphyrin π cation radical is crucial for the N-alkylation to take place. Thus, N^{21},N^{22}-etheno-bridged octaethylporphyrins (OEP) and *meso*-tetraphenylporphins (TPP) have been synthesized conveniently in yields of 44–90% by the treatment of the Co(II) porphyrins with various alkynes (acetylene, 1-hexyne, propargyl alcohol, 2-butyne-1,4-diol, phenylacetylene, diphenylacetylene, di-*o*-tolylacetylene, methyl propiolate, and dimethyl acetylenedicarboxylate) in the presence of ca. 5 equiv of ferric salts at room temperature.

Introduction

N-Alkylporphyrins have been shown to be produced in a biochemical monooxygenation process catalyzed by cytochrome P-450 enzymes.[2] This suicidal inactivation of cytochrome P-450 has been widely recognized as a useful probe for the reaction mechanism of these monooxygenases.[3] Until these findings, N-alkylation of porphyrins has never drawn general interest and relied on the reaction of free-base porphyrins with alkylating agents such as alkyl halides.[4] This approach to *N*-alkylporphyrins suffered from the low reactivity of the porphyrin nitrogen and from polyalkylation under the drastic reaction conditions that are required to achieve N-alkylation. An organometallic approach to these compounds has improved this situation. Since Johnson and his colleagues had reported that insertion of a carbene into a metal–nitrogen bond of a metalloporphyrin takes place and the resulting organometallic porphyrins can be converted into N-substituted porphyrins,[5] various N-substituted porphyrins have been prepared by the selective metal–carbon bond cleavage of the N,metal-bridged metal(III) porphyrins and by the oxidative metal-to-nitrogen alkyl shift of (σ-alkyl)iron(III) and (σ-alkyl)cobalt(III) porphyrins.[5,6] In general, *N*-alkylporphyrins are quite unique in that an *N*-alkyl group distorts a porphyrin ring from planarity and raises the basicity of the porphyrin nitrogens. As a consequence, for example, the rate of metalation and demetalation of *N*-alkylporphyrins is greatly enhanced by a factor of 10^5 in comparison with ordinary porphyrins to allow for some medical applications.[7] Thus, it is of interest to create new porphyrins with functions based on the N-substitution.

It was suggested that cytochrome P-450 is efficiently inactivated with 1-aminobenzotriazole to lead to the accumulation of an *N,N′-o*-phenylene-bridged porphyrin in hepatic tissue.[8] These novel N,N′-bridged porphyrins are generally difficult to synthesize but are of special interest due to their extraordinarily strained molecular structure[6e] and novel reactivities.[9] Thus far, N^{21},N^{22}-bridged porphyrins with a one-carbon bridge[5,6h,10] and with a two-carbon bridge[6e–g] have been prepared by (i) the reaction

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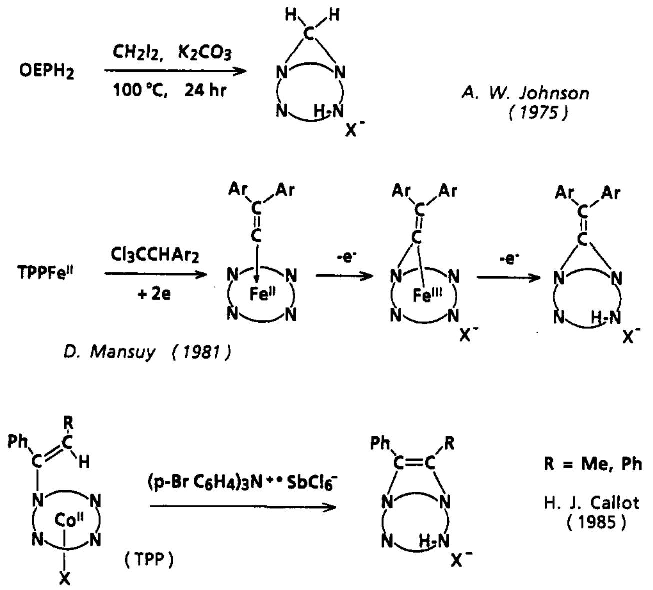
Scheme I



of free-base porphyrins with polyhalides under basic conditions, (ii) the reaction of metalloporphyrins with carbenes followed by oxidative rearrangement, and (iii) the oxidation of cobalt(II) *N*-vinyl- and *N*-phenylporphyrins. It has also been demonstrated that the treatment of (TPP)Co^{III}Cl with 1-aminobenzotriazole under aerobic conditions could give an N^{21},N^{22}-*o*-phenylene-bridged porphyrin.[6e] However, each method is restricted to only a few examples with relatively low yields. We have designed a model reaction for the P-450 inactivation process with 1-aminobenzotriazole that oxidatively gives rise to benzyne as a reactive intermediate. That is, the combination of an alkyne and an easily obtainable cobalt(III) porphyrin π cation radical in place of a benzyne and a high-valent heme intermediate that is now believed to be an iron(IV) porphyrin π cation radical, respectively, did result in the formation of an N^{21},N^{22}-etheno bridge in moderate to high yields. This paper describes a convenient preparation of the N^{21},N^{22}-etheno-bridged porphyrins based on the reaction of cobalt porphyrins with alkynes and the first isolation of novel *N*,*Co*-etheno-bridged Co(III) porphyrins that can be considered to be intermediates to N^{21},N^{22}-etheno-bridged porphyrins.[11]

Results and Discussion

***N*,*Co*-Etheno-Bridged Porphyrins and Oxidative Co-to-N Migration.** Diaquo(octaethylporphyrinato)cobalt(III) perchlorate, (OEP)Co^{III}(H$_2$O)$_2$ClO$_4$ (**1a**), in CH$_2$Cl$_2$ solution reacts immediately with various alkynes. While alkynes without electron-withdrawing substituents did not give thermally stable reaction products, dimethyl acetylenedicarboxylate (DMAD; 5 equiv) slowly converted **1a** in 2 h into a stable product, **2a**, in 83% yield after chromatographic purification on silica gel. The reaction of **1a** with methyl propiolate was completed in a few minutes to give, almost quantitatively, **3a**, which shows spectroscopic properties similar to those of **2a** but decomposed during chromatography. In the UV–vis spectrum of **2a**, the Soret band has a tailing beyond 480 nm making a rather featureless plateau up to 600 nm. This is characteristic of N,Co-bridged (OEP)Co^{III} complexes.[5,6f,12] The signal pattern for the porphyrin ligand in the ^{1}H and ^{13}C NMR spectra of **2a** and **3a** is in accord with C_s symmetry with one mirror plane along a N–Co bond. ^{1}H absorptions associated with the original alkyne moiety undergo considerable upfield shifts due to the ring current effect of the porphyrin. The two carbomethoxy groups of **2a** resonate at δ 2.39 and 1.72, and the higher field one coincides with the position of the carbomethoxy absorption of **3a**. This suggests that the carbomethoxy group of **3a** is located over the central area of the porphyrin ring. These data are consistent with the N,Co-bridged structure in which a carbon–carbon triple bond undergoes formal [2 + 2] addition to a N–Co bond with the carbomethoxy group directed toward the cobalt side. Only one ^{13}C resonance was observed for the two bridging vinylic carbon atoms in these compounds. This resonance is associated with the carbon bound to a porphyrin nitrogen because ^{13}C signals due to the cobalt-bound carbons are generally broad and frequently unobservable due to spin–spin coupling with the ^{59}Co nucleus ($I = ^7/_2$), which is quadrupolar.[13] In fact, line broadening was noted for ^{13}C signals of organocobaloximes[14] and for ^{1}H signals of organocobalt(III) porphyrins.[15] A ^{1}H–^{13}C correlation NMR experiment shows that the bridge vinyl proton (δ –0.81) of **3a** is connected to the bridge vinyl carbon, which gives a sharp signal at 122.5 ppm. Therefore, it was confirmed that the cobalt-bound carbon, which would not give a ^{13}C signal, is substituted with a carbomethoxy group in the complex **3a**.

It has been reported that *N*,*Fe*- and *N*,*Co*-methano-bridged porphyrins are oxidatively transformed into the corresponding N^{21},N^{22}-methano-bridged porphyrins.[5,6h] **2a** and **3a** were similarly converted into the N^{21},N^{22}-bridged porphyrin hydroperchlorates **4a** and **5a** in 82% (based on **2a**) and 45% (based on **1a** without isolation of **3a**) yields, respectively, by treatment with FeCl$_3$ (ca. 20 equiv) and then 10% aqueous HClO$_4$ solution. **4a** was also obtained by controlled-potential electrolysis at +1.4 V (vs Ag/AgCl) in CH$_2$Cl$_2$ with tetra-*n*-butylammonium perchlorate (TBAP) as an electrolyte. The rhodo-type visible absorption bands of **4a** and **5a** and the molecular symmetry shown by the NMR spectra are characteristic of N^{21},N^{22}-bridged porphyrins in which two adjacent nitrogens are bridged not by a vinylidene carbene[6h] but by a vinylene group.[6e,f] That is, only one ^{13}C signal (119.09 ppm) was observed for the two carbon atoms derived from the acetylenic carbons of DMAD in the NMR spectra of **4a** and the UV–vis spectra of **4a** and **5a** are much more like that of [N^{21},N^{22}-(1,2-diphenyletheno)OEP]HClO$_4$ than that of [N^{21},N^{22}-(diarylvinylideno)OEP]HClO$_4$.[6e,h] While treatment of diaquo(*meso*-tetraphenylporphyrinato)cobatl(III) perchlorate, (TPP)Co^{III}(H$_2$O)$_2$ClO$_4$ (**1b**), with DMAD and methyl propiolate afforded the *N*,*Co*-etheno-bridged complexes **2b** and **3b**, respectively, the corresponding N^{21},N^{22}-etheno-bridged (TPP)HClO$_4$ could not be obtained by treatment with FeCl$_3$ due to the higher oxidation potential of these TPP analogues.

An N,Co-bridged structure with a vinylidene carbene

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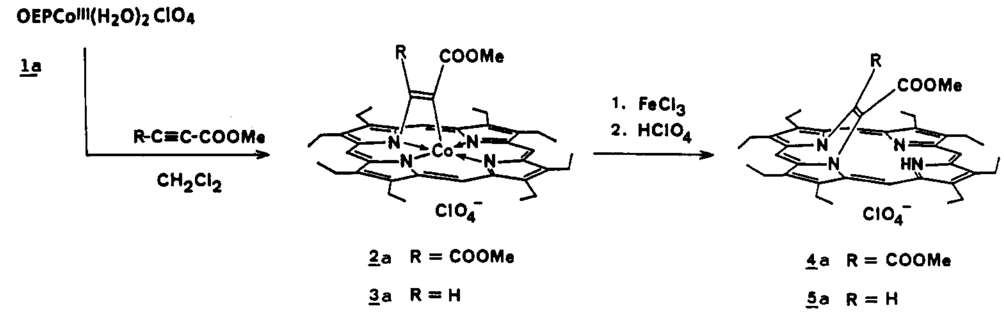
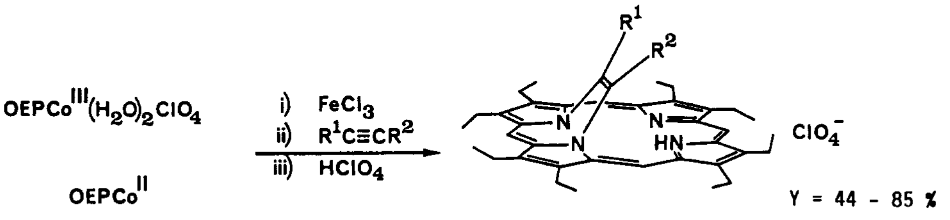
Scheme II



Scheme III



Y = 44 - 85 %

	6a	7a	8a	9a	10a	11a	12a
R^1	H	H	H	CH$_2$OH	H	C$_6$H$_5$	o-C$_6$H$_4$CH$_3$
R^2	H	n-C$_4$H$_9$	CH$_2$OH	CH$_2$OH	C$_6$H$_5$	C$_6$H$_5$	o-C$_6$H$_4$CH$_3$

inserted into an N–Co bond is also an alternative possibility that is compatible with the spectral data of **2a** and **3a** if the alkynes could be isomerized to vinylidene carbenes through a 1,2-shift of the carbomethoxy group during the reaction with **1a**. However, the fact that the N^{21},N^{22}-bridged porphyrins derivatized oxidatively from **2a** and **3a** do not have such a vinylidene carbene bridge but an etheno bridge clearly precludes such a hypothesis.

Metalloporphyrins with a bridged structure between the central metal and one of the four pyrrole nitrogens are of interest, since an iron(III) porphyrin with an oxygen atom inserted into an N–Fe bond is postulated as one of the possible structures for the highly oxidized forms of some hemoproteins. Thus, bridged metalloporphyrins with a metal–O–N linkage (metal = Cu,[16] Ni,[17] Fe[18]), with a metal–N–N linkage (metal = Zn,[19] Ni,[20] Fe[21]), with a metal–C–N linkage (metal = Ni,[22] Fe,[6h,j,23] Co[5,6f,12a]), and with a metal–O–C–C–N linkage (metal = Fe,[3a,6i,24] Co[12b,25]) have so far been reported. Although a similar *N,Co*-etheno-bridged intermediate was postulated by Callot et al.,[6e] **2a,b** and **3a,b** are the first isolated examples of metal,N-(two-carbon)-bridged metalloporphyrins.

Synthesis of N^{21},N^{22}-Etheno-Bridged Porphyrins. The formation of N^{21},N^{22}-bridged porphyrins through the oxidation of N,metal-bridged metalloporphyrins has been limited to a diarylvinylideno bridge[6h] and a carboalkoxymethano bridge.[5] The present alkyne addition–Fe(III) oxidation reaction sequence cannot be regarded as a versatile synthetic method for N^{21},N^{22}-bridged porphyrins either, because *N,Co*-etheno-bridged porphyrins are not available unless the alkyne is conjugated with a carbonyl group. However, we have found that the reaction of Co(III) porphyrins with alkynes in the presence of an oxidizing agent results in the formation of various N^{21},N^{22}-etheno-bridged porphyrins directly in moderate to good yields irrespective of the substituents on the alkyne and on the porphyrin periphery. N^{21},N^{22}-etheno-bridged porphyrins were previously reported by two groups.[6e,f] Callot et al. oxidized Co(II) *N*-vinylporphyrins or (σ-vinyl)Co(III) porphyrins with aminium cation radicals to lead to N^{21},N^{22}-etheno-bridged porphyrins. However, the vinyl groups that led to successful bridging were restricted to β-substituted α-styryl groups.

When **1a** was allowed to react with ca. 5 equiv of acetylene, 1-hexyne, propargyl alcohol, 2-butyne-1,4-diol, phenylacetylene, diphenylacetylene, and di-*o*-tolylacetylene in the presence of FeCl$_3$ (1–2 equiv) in CH$_2$Cl$_2$ at ambient temperature for 2 h, N^{21},N^{22}-etheno-bridged (OEP)HClO$_4$ compounds (**6a**–**12a**) were obtained after workup with 10% aqueous HClO$_4$ solution followed by chromatography on silica gel as summarized in Table I. While **2a** was afforded in 59% yield when DMAD (5 equiv) was allowed to react with **1a** even in the presence of 1.2 equiv of FeCl$_3$, the use of 2.5 equiv of FeCl$_3$ resulted in the formation of **4a** in 42% yield in this one-pot procedure. ^{1}H NMR spectra showed a set of four singlets with equal intensities due to the meso protons of the porphyrin ring for **5a**, **7a**, **8a**, and **10a**, which are obtained from unsymmetrical alkynes, and a set of three singlets (1:1:2 ratio) for **4a**, **6a**, **9a**, and **11a**, which are obtained from symmetrical alkynes. The singlet at around δ −2, which is assigned to the bridge vinyl proton,

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Table I. Yields and ^{1}H NMR Data for N,Co- and N^{21},N^{22}-Bridged Porphyrins[a]

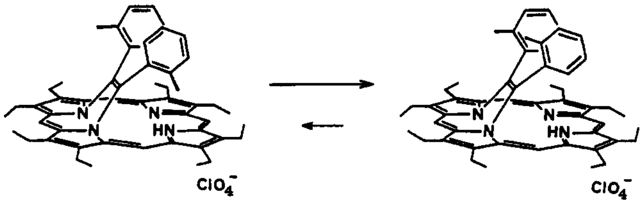
				^{1}H chem shift, δ			
compd	R^1	R^2	yield, %	meso H	vinyl H	other R^1 (R^2)	N–H
2a	CO_2Me	CO_2Me	83	10.53 (2 H), 10.18 (2 H)		2.39 (3 H), 1.72 (3 H)	
3a	CO_2Me	H		10.54 (2 H), 10.21 (2 H)	–0.81 (1 H)	1.72 (3 H)	
4a	CO_2Me	CO_2Me	82	10.96 (1 H), 10.73 (2 H), 10.38 (1 H)		1.92 (6 H)	–3.95
5a	CO_2Me	H	45[b]	10.95 (1 H), 10.74 (1 H), 10.71 (1 H), 10.29 (1 H)	–1.67 (1 H)	1.48 (3 H)	–4.08
6a	H	H	52, 78[c]	10.86 (1 H), 10.58 (2 H), 10.22 (1 H)	–2.57 (2 H)		–3.90
7a	H	*n*-Bu	50	10.78 (1 H), 10.72 (1 H), 10.61 (1 H), 10.22 (1 H)	–2.46 (1 H)	–0.31 (t, 3 H), –0.86 (m, 2 H), –1.72 (m, 1 H), –2.17 (m, 1 H), –3.63 (m, 1 H), –4.10 (m, 1 H)	–4.00
8a	H	CH_2OH	48	10.81 (1 H), 10.76 (1 H), 10.53 (1 H), 10.20 (1 H)	–2.15 (1 H)	–1.59 (m, 1 H), –2.02 (m, 1 H)	–4.00
9a	CH_2OH	CH_2OH	50, 78[c]	10.83 (1 H), 10.79 (2 H), 10.21 (1 H)		0.58 (d, 2 H, J_{vic} = 11.0 Hz), –0.41 (d, 2 H, J_{gem} = 14.3 Hz), –2.35 (dd, 2 H)	–4.08
10a	H	Ph	44	11.02 (1 H), 10.67 (1 H), 10.34 (1 H), 10.30 (1 H)	–2.32 (1 H)	6.08 (t, 1 H), 5.63 (t, 2 H), 1.95 (d, 2 H)	nd[h]
11a	Ph	Ph	71, 84[c]	11.21 (1 H), 10.52 (1 H), 10.28 (2 H)		6.12 (t, 2 H), 5.69 (t, 4 H), 2.30 (br, 4 H)	–3.41
12a	*o*-Tol	*o*-Tol	85[d]	11.13 (1 H), 10.46 (1 H), 10.28 (2 H)		5.99 (t, 2 H), 5.85 (d, 2 H), 5.03 (t, 2 H), 0.42 (d, 2 H), 0.38 (6 H)	–3.22
12a′	*o*-Tol	*o*-Tol		11.20 (1 H), 10.55 (1 H), 10.42 (1 H), 10.27 (1 H)		6.19 (m, 2 H), 6.11 (t, 1 H), 5.76 (d, 1 H), 5.44 (t, 1 H), 5.22 (d, 1 H),[e] 0.11 (3 H), –2.89 (3 H)	

compd	R^1	R^2	yield, %	pyrrole β-H	vinyl H	R^1 (R^2)	N–H
2b	CO_2Me	CO_2Me	74	9.09, 8.74 (2 H × 2); 9.03, 8.96 (d × 2, 2 H × 2)		2.63 (3 H), 1.98 (3 H)	
3b	CO_2Me	H		9.32, 8.78 (2 H × 2); 8.96, 8.78 (d × 2, 2 H × 2)	0.04 (1 H)	2.01 (3 H)	
6b	H	H	66	8.99, 8.95, 8.93, 8.78 (d × 4, 2 H × 4)	–1.68 (2 H)		nd
7b	H	*n*-Bu	47	9.05, 9.02, 9.00, 8.99, 8.97, 8.87, 8.86, 8.74, (d × 8, 1 H × 8)	–1.38 (1 H)	–0.10 (t, 3 H), –0.56 (m, 2 H), –1.29 (m, 1 H), –1.72 (m, 1 H), –2.99 (m, 1 H), –3.73 (m, 1 H)	nd
8b	H	CH_2OH	67	9.05, 9.04, 9.02, 9.00, 8.96, 8.90, 8.84, 8.71 (d × 8, 1 H × 8)	–1.28 (1 H)	0.66 (dd, 1 H, J_{vic} = 9.2 Hz), –1.08 (dd, 1 H, J_{vic} = 4.0 Hz), –1.71 (dd, 1 H, J_{gem} = 14.0 Hz)	–3.3
9b	CH_2OH	CH_2OH	75[f]	9.06, 9.02, 8.92, 8.79 (d × 4, 2 H × 4)		1.29 (d, 1 H, J_{vic} = 9.2 Hz), 0.28 (d, 1 H, J_{gem} = 14.5 Hz), –2.30 (dd, 1 H)	–3.1
10b	H	Ph	45	9.24, 9.22, 9.03, 9.02, 8.97, 8.88, 8.85, 8.56 (d × 8, 1 H × 8)	–1.48 (1 H)	6.21 (t, 1 H), 5.83 (t, 2 H), 2.33 (d, 2 H)	–3.1
11b	Ph	Ph	90[f]	9.21, 9.15, 8.82, 8.77 (d × 4, 2 H × 4)		6.34 (dd, 2 H), 5.93 (br, 4 H), 2.65 (br, 4 H)	–2.7
14b	CH=CH-Cl		29[g]	8.82, 8.60 (1 H × 2); 8.46, 7.79 (d × 2, 2 H × 2)	2.29 (d, 1 H, *J* = 12.2 Hz), –1.46 (d, 1 H)		nd

[a] Absorptions due to peripheral ethyl groups at δ 4 and 2 and meso phenyl groups at around δ 8 were omitted. The chemical shifts are measured in $CDCl_3$. Doublet, double doublet, triplet, multiplet, and broad absorption are abbreviated as d, dd, t, m, and br. The notation for singlet is omitted. [b] Based on **1a**. [c] The reaction yield with 20 equiv of $FeCl_3$. [d] Total yield for the two isomers. [e] Two aromatic protons could not be specified. [f] The reaction yield with $Fe(ClO_4)_3$. [g] Obtained as a mixture with 47% yield of **6b** (see text). [h] nd = not determined.

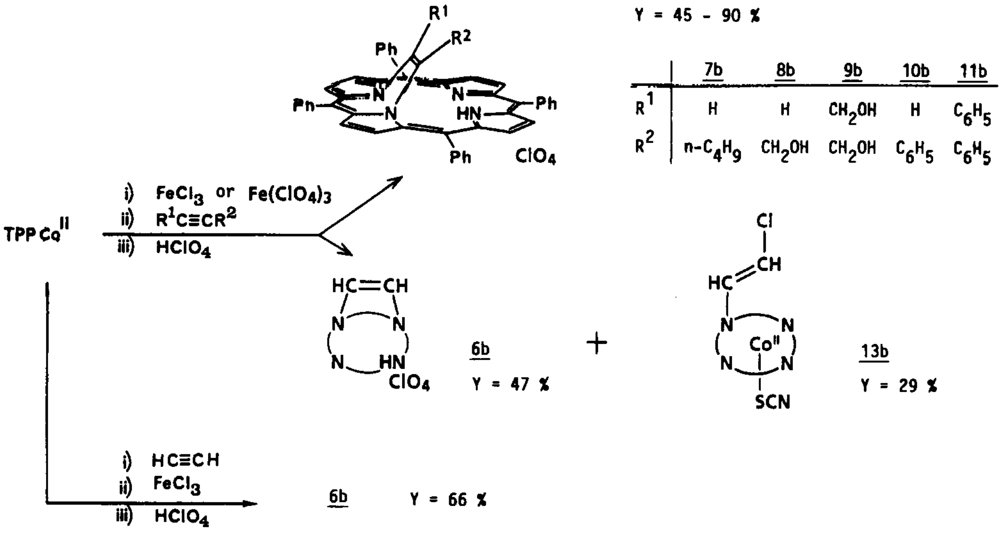
is observed for the products obtained from terminal alkynes (**5a**, **6a**, **7a**, **8a**, and **10a**) but not for those from disubstituted alkynes (**4a**, **9a**, and **11a**). The upfield shifts of the ^{1}H NMR signals due to the original alkyne moiety and the splitting pattern of the absorption due to the porphyrin moiety are completely consistent with the structure in which the adjacent two nitrogens of the porphyrin are bridged by a 1,2-etheno group. [N^{21},N^{22}-(1,2-di-*o*-tolyletheno)OEP]$HClO_4$ was obtained as a mixture of two rotational isomers in a ratio of 1:1, as evidenced by the appearance of two sets of ^{1}H NMR signals just after chromatographic purification. The C_s-symmetric isomer **12a** shows one absorption due to the *o*-tolyl methyl groups at δ 0.38, while the dissymmetric isomer **12a′** shows two absorptions at δ –2.89 and 0.11, which correspond to the methyl groups directed to the center and to the periphery of the porphyrin ring, respectively. When the original mixture was allowed to stand in chloroform solution at room temperature overnight, these signals converged to that of the thermally more stable C_s-symmetric isomer in which the *o*-tolyl methyl groups take the outside position of the porphyrin ring. This restricted rotation of the bridge aryl groups is also occurring with **11a**, because the ortho

Scheme IV



12a′ 12a

Scheme V



Y = 45 - 90 %

	7b	8b	9b	10b	11b
R^1	H	H	CH_2OH	H	C_6H_5
R^2	n-C_4H_9	CH_2OH	CH_2OH	C_6H_5	C_6H_5

proton NMR resonance of the bridge phenyl groups of **11a** appears as a very broad absorption at around 2 ppm.

Free bases of **4a–12a** turned out to be difficult to isolate due to decomposition during neutralization, as is frequently seen for N,N′-disubstituted porphyrins.[5,6e,g,h,10] If the treatment with perchloric acid was omitted in the workup process of the reaction with diphenylacetylene, the product **11a′** showed a UV–vis spectrum identical with that of **11a** and ESR signals consistent with a high-spin Fe(III) at g = 4.30 and 1.91 at 77 K in CH_2Cl_2. The magnetic moment measured by the Evans method in $CDCl_3$ (5.08 μ_B) is compatible with a high-spin Fe(III). The microanalysis agreed with the composition [N^{21},N^{22}-(1,2-diphenyletheno)OEP]$HFeCl_4$. Thus, N^{21},N^{22}-bridged OEP seems to be protonated, taking ferric tetrachloride as a counteranion under the reaction conditions.

(OEP)Co^{II} can be utilized conveniently for the direct preparation of **4a–12a** without reduction of the yields if an additional amount of ferric salts is used to oxidize Co(II) to Co(III) in situ. The best result was obtained when alkynes were allowed to react with the filtered solution from the vigorously stirred mixture of (OEP)Co^{II} and $FeCl_3$ (20 equiv) in CH_2Cl_2. Thus, **6a**, **9a**, and **11a** were prepared in 78, 78, and 84% yields, respectively, by this method as shown in Table I. The reaction of (TPP)Co^{II} with 1-hexyne, propargyl alcohol, 2-butyne-1,4-diol, phenylacetylene, and diphenylacetylene in the presence of ferric salts took place analogously at room temperature in CH_2Cl_2 solution to give N^{21},N^{22}-etheno-bridged (TPP)$HClO_4$ (**7b–11b**) in moderate to high yields. Although both $FeCl_3$ and $Fe(ClO_4)_3{\cdot}6H_2O$ are equally effective for the reaction of (OEP)Co^{II} with various alkynes, $FeCl_3$ was found to be suitable for the reaction of (TPP)Co^{II} with terminal alkynes and $Fe(ClO_4)_3{\cdot}6H_2O$ for the reaction of (TPP)Co^{II} with disubstituted alkynes. While the introduction of acetylene gas into a well-stirred mixture of (TPP)Co^{II} and $FeCl_3$ in CH_2Cl_2 resulted exceptionally in the formation of a considerable amount of the byproducts [N-(β-chlorovinyl)TPP]Co^{II}SCN (**13b**; after treatment with NaSCN) and its free base **14b**, addition of $FeCl_3$ to a vigorously stirred CH_2Cl_2 solution of (TPP)Co^{II} under an acetylene gas atmosphere gave rise to [N^{21},N^{22}-(etheno)-TPP]$HClO_4$ (**6b**) in 66% yield without those byproducts. **6b–11b** could be characterized easily on the basis of the spectral data, which are comparable with those of the corresponding OEP analogues **6a–11a**. **13b**, which showed rhodo-type visible absorption bands and sharp paramagnetic NMR signals characteristic of Co(II) N-substituted porphyrins, was demetalated with trifluoroacetic acid in CH_2Cl_2 to give **14b** quantitatively. The N-(β-chlorovinyl) group of **14b** shows two ^{1}H NMR signals due to the vinylic protons at 2.29 and −1.46 ppm with a vicinal coupling constant (12.2 Hz) in the range of trans coupling.

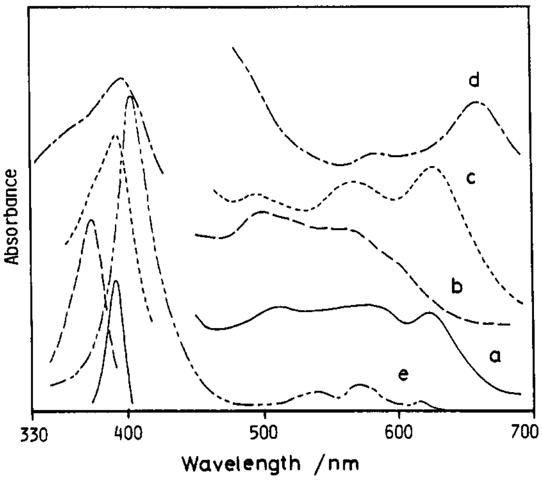


Figure 1. UV–vis spectra of Co^{III}(OEP) π cation radicals: in CH_2Cl_2: (a, —) **15a**; (b, --) **19a**; (c, ---) **18a**; (d, -·-) **16a**; (e, -·-·) N^{21},N^{22}-bridged (OEP)$HClO_4$ (**11a**).

Reaction Mechanism. In order to provide more insight into the mechanism in the above reaction, the reactions of (OEP)Co^{II} and (OEP)Co^{III} complexes with various oxidizing agents in CH_2Cl_2 were monitored by visible spectroscopy and then the reaction behaviors of the resulting oxidized species toward diphenylacetylene were investigated. Oxidation of **1a** with a large excess amount of $Fe(ClO_4)_3{\cdot}6H_2O$ proceeded with continuing isosbestic points at 385 and 567 nm. The ultimate spectrum was identical with that of the π cation radical [(OEP)$^{\bullet+}$]-$Co^{III}(ClO_4)_2$ (**15a**), which was prepared by electrochemical oxidation of (OEP)Co^{II} at +1.2 V vs Ag/AgCl in the presence of TBAP (Figure 1a).[26] The oxidation of (OEP)Co^{III}Cl with a limited amount of Cl_2 gas caused the visible spectral change with isosbestic points at 491 and 578 nm, leading to the spectrum that is associated with the π cation radical [(OEP)$^{\bullet+}$]$Co^{III}Cl_2$ (**16a**; Figure 1d).

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[26] Dolphin, D.; Forman, A.; Borg, D. C.; Fajer, J.; Felton, R. H. *Proc. Natl. Acad. Sci. U.S.A.* **1971**, *68*, 614–618.

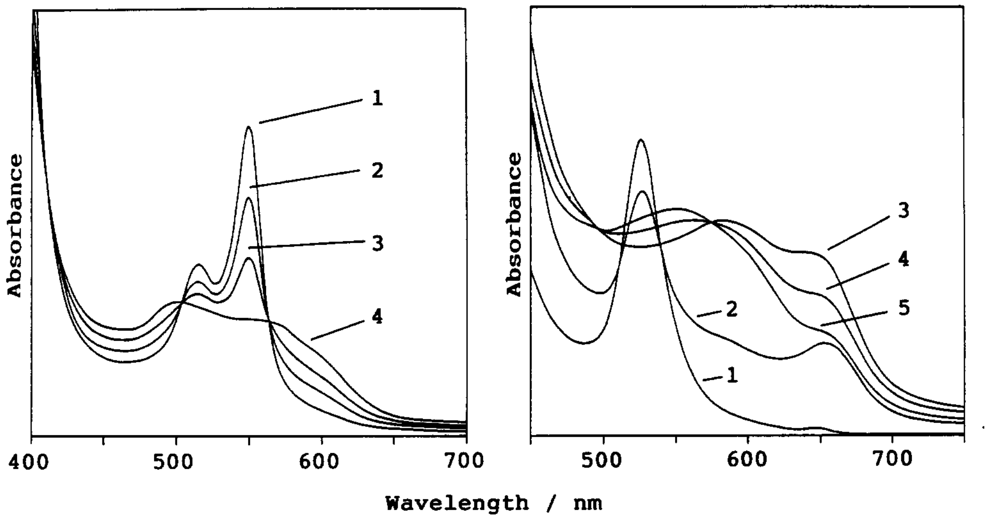
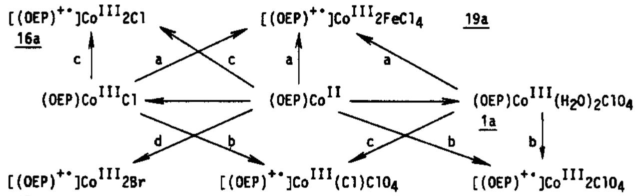


Figure 2. Visible spectral changes during $FeCl_3$ oxidation in CH_2Cl_2: (left) line 1 ($\mathrm{(OEP)Co^{II}}$) → line 2 → line 3 → line 4 (π cation radical); (right) line 1 ($\mathrm{(TPP)Co^{II}}$) → line 2 → line 3 (π cation radical) → line 4 → line 5 (π dication).

This spectrum is virtually the same as that of $\mathrm{[(OEP)^{\bullet+}]Co^{III}Br_2}$ (**17a**), which was prepared by the treatment of $\mathrm{(OEP)Co^{II}}$ with an equimolar amount of Br_2.[26] **15a** and **16a** are also prepared by starting from $\mathrm{(OEP)Co^{II}}$. The oxidation of **1a** with Cl_2 gave rise to a complex which shows the same spectrum as that obtained by treating $\mathrm{(OEP)Co^{III}Cl}$ with $\mathrm{Fe(ClO_4)_3{\cdot}6H_2O}$ (Figure 1c). In the latter case, three isosbestic points were observed at 428, 494, and 575 nm throughout the oxidation. Since the absorption maxima of Figure 1c appear between those of **15a** and **16a**, this oxidized species is reasonably associated with the π cation radical with mixed axial ligands $\mathrm{[(OEP)^{\bullet+}]Co^{III}(Cl)ClO_4}$ (**18a**). Oxidation of $\mathrm{(OEP)Co^{II}}$ with $FeCl_3$ caused the spectral change to a blue-shifted Soret band at 374 nm with a remarkably diminished intensity and a featureless visible band characteristic of π cation radicals (Figure 1b) with isosbestic points at 410, 504, and 563 nm throughout the oxidation as shown in Figure 2 (left). Since all the species generated by treatment of **1a**, $\mathrm{(OEP)Co^{II}}$, and $\mathrm{(OEP)Co^{III}Cl}$ with $FeCl_3$ showed the Soret bands at the same wavelength, they are considered to be the Co(III) porphyrin π cation radicals **19a** with a noncoordinating counteranion such as $\mathrm{(Fe^{III}Cl_4)^-}$. It is reasonable that the Soret and the visible bands move monotonously to shorter wavelength with a decreasing axial ligand field of $\mathrm{Co^{III}(OEP)}$ π cation radicals: 2 Cl^- (**16a**) = 2 Br^- (**17a**) > $Cl^-ClO_4^-$ (**18a**) > 2 ClO_4^- (**15a**) > 2 $FeCl_4^-$ (**19a**). Whereas **19a** was generated in the presence of a large excess amount of anhydrous $FeCl_3$, **15a** and **18a** were prepared with $\mathrm{Fe(ClO_4)_3{\cdot}6H_2O}$. Thus, water molecules would occupy axial coordination sites of the Co(III) porphyrin π cation radicals **15a** and **18a** to account for the difference in the absorption spectra of **15a** and **19a**.

15a generated chemically by $\mathrm{Fe(ClO_4)_3{\cdot}6H_2O}$ or electrochemically reacted with diphenylacetylene to give **11a** in 57% or 47% yield, respectively. This indicates that there is no critical role for Fe besides oxidation. In fact, there was no N-alkylated porphyrin formed when $\mathrm{(OEP)Fe^{III}ClO_4}$ and $\mathrm{(OEP)H_2}$ were treated with diphenylacetylene in the presence of $FeCl_3$ or $\mathrm{Fe(ClO_4)_3{\cdot}6H_2O}$ in control experiments. Furthermore, both **18a** and **19a** also afforded **11a** in similar yields (50–90%). In contrast to the case for the Co(III) porphyrin π cation radicals with a weakly coordinating axial ligand, **17a** did not react with diphenylacetylene. Thus, it is concluded that Co(III) porphyrin π cation radicals react with alkynes and the vacancy in the axial coordination site of the Co(III) porphyrin π cation radical is crucial for the N-substitution reaction to take place. Therefore, we assume the intermediacy of organocobalt(III) porphyrin complexes such as an acetylene π complex of a Co(III) porphyrin π cation radical (A) and an *N*,*Co*-etheno-bridged Co(III) porphyrin π cation radical (B). As both intermediates can be regarded formally as Co(IV) porphyrin complexes, they would rearrange to N^{21},N^{22}-etheno-bridged Co(II) porphyrin complexes (C) via reductive elimination with both N–Co and C–Co bond breakage and new N–C bond formation. The intermediate C could not be obtained due to fast demetalation, as is generally the case with N,N′-disubstituted porphyrins.[10a] The cyclic voltammogram of **2a** exhibits a single reversible wave at $E_{1/2}$ = +0.65 V in CH_2Cl_2 vs the Ag/AgCl couple. This suggests that a one-electron-oxidized species of **2a**, which can be assumed to be the corresponding π-cation radical B, is relatively stable. When $\mathrm{Co^{III}(OEP)}$ π cation radicals react with alkynes, similar oxidized intermediates (B) would be formed as an initial step and then they would rearrange into N^{21},N^{22}-bridged $\mathrm{(OEP)Co^{II}}$ complexes (C) or be reduced to N,Co-bridged $\mathrm{(OEP)Co^{III}}$ complexes. The latter electron-transfer pathway is preferred in the case of alkynes with electron-withdrawing substituents which strengthen the oxidizing power of the N,Co-bridged $\mathrm{Co^{III}(OEP)}$ π cation radical (B) and at the same time destabilize the transition state for the rearrangement that requires a formal charge transfer from the etheno moiety to Co(III).

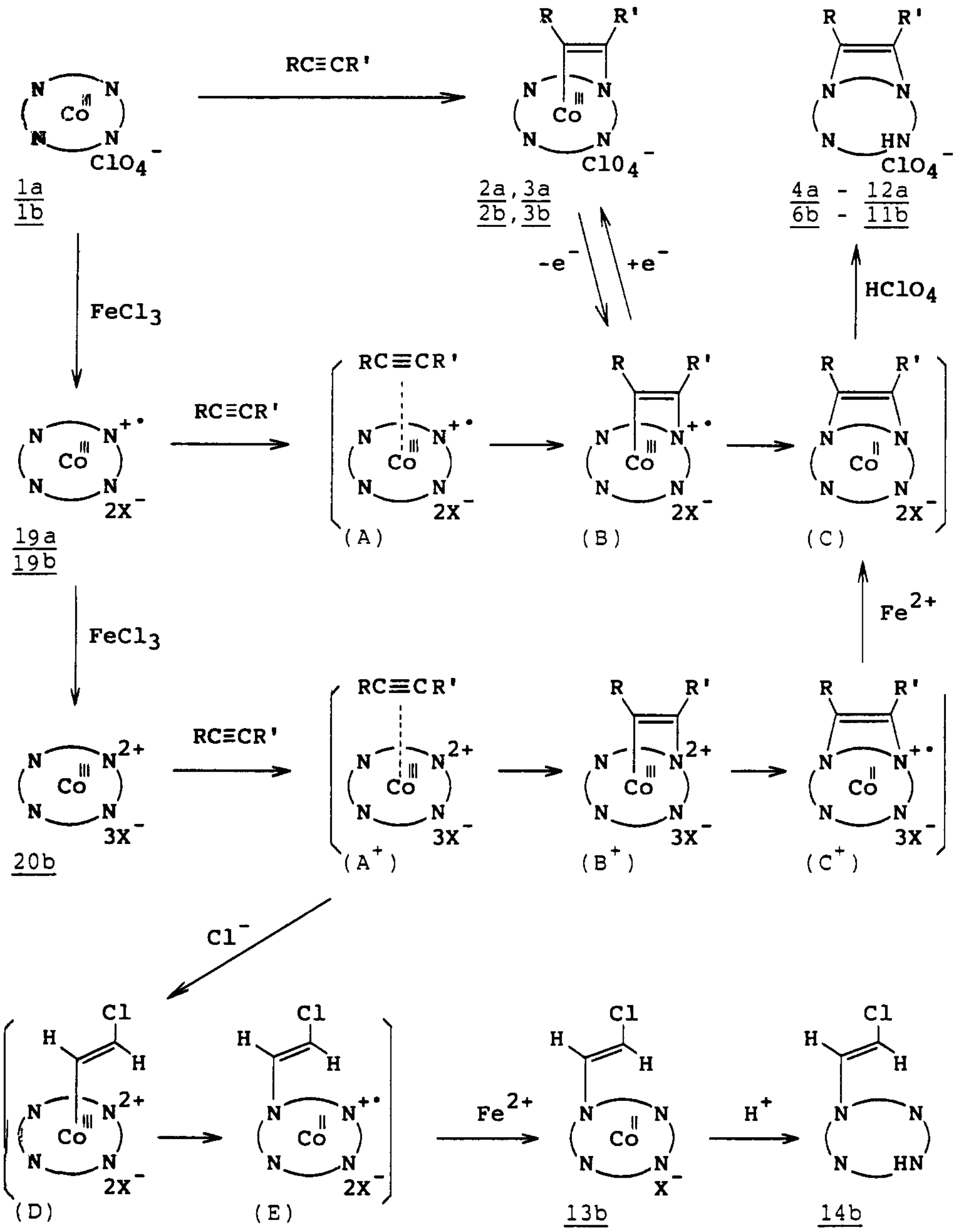
Scheme VI



reagents: a) $FeCl_3$; b) $\mathrm{Fe(ClO_4)_3{\cdot}6H_2O}$; C) Cl_2; d) Br_2

Although $\mathrm{Co^{III}(OEP)}$ π cation radical **19a** was quite stable even in the presence of excess $FeCl_3$ (Figure 2, left), the UV–vis spectral change during the oxidation of $\mathrm{(TPP)Co^{II}}$ with excess $FeCl_3$ showed that the initially generated $\mathrm{Co^{III}(TPP)}$ π cation radical **19b** (λ_{max} 399, 533, 650 nm; see Figure 2, right, line 3) was further oxidized to

Scheme VII



Co^{III}(TPP) π dication **20b** (Figure 2, right, line 5). This is in agreement with the result for the electrochemical oxidation of (TPP)Co^{II}.[27] Therefore, π dication **20b** is formed when a mixture of (TPP)Co^{II} and Fe(III) salt is allowed to react well, and *N*-(β-chlorovinyl)porphyrin **13b** is produced by the reaction of π dication **20b** with acetylene. On the other hand, π cation radical **19b** reacts with acetylene too fast to allow further oxidation to **20b** when $FeCl_3$ is added to the mixture of (TPP)Co^{II} and acetylene. In this case, **13b** is not obtained. This phenomenon is rationalized in terms of the competition between a porphyrin nitrogen and a chloride ion when a Co(III) acetylene π complex intermediate (A or A⁺) undergoes nucleophilic attack at the acetylene ligand to lead to a *N*,*Co*-etheno-bridged complex (B or B⁺) and a (σ-β-chlorovinyl)Co^{III} complex (D), respectively, because the π-complexed acetylene of A or A⁺ would have partial cationic charge as a form of Co^{III}–CH=CH⁺ through σ-π conjugation. Since the porphyrin nitrogen of the π dication A⁺ should be less nucleophilic than that of the π cation radical A, the chloride ion can compete well with the porphyrin nitrogen of the π dication A⁺ to give the (σ-β-chlorovinyl)Co^{III} π dication D. This intermediate spontaneously undergoes Co-to-N migration of the vinyl ligand to give the [*N*-(β-chlorovinyl)TPP]Co^{II} π cation radical E and then **13b**. Since intermolecular attack of the chloride ion would be more susceptible to steric hindrance owing to alkyne substituents than intramolecular nitrogen attack, the reaction of the π dication **20b** with disubstituted alkynes still seems to take the intramolecular course exclusively via B⁺, which rearranges to N^{21},N^{22}-etheno-bridged Co(II) porphyrin π cation radical C⁺ and then gives N^{21},N^{22}-etheno-bridged (TPP)$HClO_4$.

In conclusion, cobalt(III) porphyrin π cation radicals, which are conveniently prepared without special care against the presence of oxygen and water, react with various alkynes to allow easy access to N^{21},N^{22}-etheno-bridged porphyrins. Finally, on the basis of the above result, we point out that the formation of the *N*,*N'*-*o*-phenylene-bridged heme of cytochrome P-450 treated with

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[27] (a) Wolberg, A.; Manassen, J. *J. Am. Chem. Soc.* **1970**, *92*, 2982–2991. (b) Lin, X. Q.; Kadish, K. M. *Anal. Chem.* **1985**, *57*, 1498–1501.

1-aminobenzotriazole would be interpreted in terms of the intermediacy of the *N,Fe-o*-phenylene-bridged heme and that organoiron complexes of heme proteins should play important roles in a number of biochemical N-alkylation processes.

Experimental Section

UV–visible spectra were measured on a Shimadzu UV-245FS spectrometer. ^{1}H NMR (270 MHz) and ^{13}C NMR (67.8 MHz) spectra were recorded on a JEOL GX-270 spectrometer in $CDCl_3$. ^{1}H and ^{13}C chemical shifts are referenced with respect to tetramethylsilane (0 ppm) and $CDCl_3$ (77.05 ppm), respectively, as internal standards. Cyclic voltammetry was carried out with a YANACO VMA-010 instrument at a glassy-carbon electrode with an Ag/AgCl couple as a reference electrode and tetra-*n*-butylammonium perchlorate (TBAP) as an electrolyte in CH_2Cl_2 (scan rate 100 mV/s, scan range −0.1 to +1.8 V). Controlled-potential electrolysis was performed with a YANACO VE-9 electrolyzer at a platinum-mesh electrode. Elemental analysis of C, H, and N was performed with a YANACO CHN MT3 recorder. The iron content was determined spectrophotometrically as a ferrous complex of 1,10-phenanthroline after the sample was demetalated by 10% aqueous $HClO_4$ solution. Kieselgel 60F_{254} silica gel plates (Merck) and Wakogel C-300 silica gel (Wako Junyaku) were used for TLC and column chromatography. **1a** and **1b** were prepared according to the literature.[28]

[*N,Co*-(1,2-Dicarbomethoxyetheno)porphyrinato]cobalt(III) Perchlorates (2a,b). Five equivalents of dimethyl acetylenedicarboxylate was added to a CH_2Cl_2 solution (10 mL) of (OEP)$Co^{III}(H_2O)_2ClO_4$ or (TPP)$Co^{III}(H_2O)_2ClO_4$ (0.2 mM) under an argon atmosphere. The solution turned brown in 2 h. The solvent was removed, and then the residue was chromatographed on silica gel with CH_2Cl_2–acetone (10:1). The main fraction was recrystallized from CH_2Cl_2–hexane. Yields and ^{1}H NMR data are listed in Table I. **2a**: ^{13}C NMR CO 163.0, 148.5, py $C_{\alpha,\beta}$ 147.9, 146.8, 146.7, 146.5, 146.2, 146.1, 146.1, 142.7; N–C_{bridge} 114.6, C_{meso} 101.7, 101.2, OCH_3 50.3, 49.8, CH_2 20.9, 20.2, 19.9, 19.8, CH_3 18.3, 18.2, 17.9, 15.9 ppm; UV–vis (CH_2Cl_2) λ_{max} (log ϵ) 394 (4.72), 431 (sh) (4.52), 515 (3.50), 565 (3.40) nm. Anal. Calcd for $C_{42}H_{50}N_4O_8ClCo$: C, 60.54; H, 6.05; N, 6.72. Found: C, 60.18; H, 6.26; N, 6.52. **2b**: UV–vis (CH_2Cl_2) λ_{max} (log ϵ) 437 (4.82), 580 (3.83) nm. Anal. Calcd for $C_{50}H_{34}N_4O_8ClCo$: C, 65.76; H, 3.75; N, 6.14. Found: C, 63.90; H, 4.19; N, 6.62.

[*N,Co*-(2-Carbomethoxyetheno)porphyrinato]cobalt(III) Perchlorates (3a,b). A spectroscopically very pure sample of **3a** was formed immediately when a slight excess amount of methyl propiolate was added to a $CDCl_3$ solution (0.5 mL) of **1a** or **1b** (0.04 mM). Spectral measurements were done without further purification due to the labile nature of the compounds. **3a**: ^{13}C NMR CO 160.4, py $C_{\alpha,\beta}$ 147.8, 146.9, 146.7, 146.4, 145.9 (×2), 144.4, 144.0; N–C_{bridge} 122.5, C_{meso} 102.2, 101.1, OCH_3 49.5, CH_2 20.9, 20.2, 20.0, 19.9, CH_3 18.6, 18.2, 18.1, 16.5 ppm; UV–vis (CH_2Cl_2) λ_{max} 394, 431, 523, 565 nm. **3b**: UV–vis (CH_2Cl_2) λ_{max} 412, 548 nm.

[N^{21},N^{22}-(1,2-dicarbomethoxyetheno)OEP]$HClO_4$ (4a). (i) Chemical Oxidation of 2a. *N,Co*-Etheno-bridged porphyrin **2a** (40 mg) was dissolved in CH_2Cl_2 (20 mL). An excess amount (ca. 20 equiv) of $FeCl_3$ was added to the solution, and the reaction mixture was stirred for 1 h at ambient temperature. The solution changed from brown to a dichroic green–red. The solution was washed with 10% $HClO_4$ and then with water, dried over Na_2SO_4, and evaporated to dryness, and the residue was then chromatographed on silica gel with CH_2Cl_2–acetone (3:1). The main fraction was recrystallized from a CH_2Cl_2–ether mixture to afford **4a** in 82% yield. ^{13}C NMR CO 154.11, py $C_{\alpha,\beta}$ 150.44, 146.46, 146.35, 145.41, 144.95, 144.16, 142.95, 140.79, N–C_{bridge} 119.09, C_{meso} 102.76, 102.29, 101.72, OCH_3 51.37, CH_2 20.62, 19.88, 19.88, 19.73, CH_3 18.68, 18.37, 17.48, 17.39 ppm; UV–vis (CH_2Cl_2) λ_{max} (log ϵ) 401 (5.13), 535 (3.94), 569 (4.06), 614 (3.63) nm. Anal. Calcd for $C_{42}H_{51}N_4O_8Cl$: C, 65.06; H, 6.63; N, 7.23. Found: C, 65.24; H, 6.62; N, 7.17.

(ii) Electrochemical Oxidation of 2a. 2a (20 mg) was placed in a central region of an H-cell with three compartments separated through frits. Bulk electrolysis was carried out at a platinum-mesh electrode at +1.2–1.4 V (vs Ag/AgCl) in CH_2Cl_2 (10 mL) solution containing TBAP (ca. 0.1 M/L) under an argon atmosphere. After the solution changed to a dichroic green–red, the reaction mixture was evaporated and the residue was chromatographed on silica gel with CH_2Cl_2. As the product was not separable completely from TBAP, the yield was calculated to be 40% with the aid of the UV–vis spectral data of the authentic sample.

[N^{21},N^{22}-(Carbomethoxyetheno)OEP]$HClO_4$ (5a). 1a (130 mg) was dissolved in CH_2Cl_2 (20 mL), and a slight excess of methyl propiolate was added. The solution turned to brown immediately. $FeCl_3$ (20 equiv) was added to the solution, and the reaction mixture was stirred for 2 h at ambient temperature. The workup was done in the same way as for **4a** to give **5a** in 45% yield based on **1a**: UV–vis (CH_2Cl_2) λ_{max} (log ϵ) 402 (5.05), 537 (3.92), 573 (4.03), 620 (3.21) nm. Anal. Calcd for $C_{40}H_{49}N_4O_6Cl$: C, 66.98; H, 6.89; N, 7.81. Found: C, 66.92; H, 6.84; N, 7.72.

N^{21},N^{22}-Bridged (OEP)$HClO_4$ (6a–12a). (i) Reaction of 1a with Alkynes in the Presence of $FeCl_3$. CH_2Cl_2 (10 mL) and alkyne (5–10 equiv) were added successively to a flask charged with **1a** (150 mg) and $FeCl_3$ (2 equiv) under argon. The solution changed to reddish green immediately. The reaction mixture was stirred for 4 h at room temperature and then evaporated. The residue was dissolved in acetone and the solution quickly passed through a short silica gel column in order to remove inorganic salts. A $CHCl_3$ solution of the reaction product was then washed with 10% $HClO_4$ and water repeatedly. Column chromatography on silica gel with CH_2Cl_2–acetone (10:1) followed by recrystallization from CH_2Cl_2–ether or CH_2Cl_2–*n*-hexane afforded N^{21},N^{22}-bridged (OEP)$HClO_4$ in the yields listed in Table I. **6a**: ^{13}C NMR py $C_{\alpha,\beta}$ 150.10, 146.39, 146.08, 144.87, 142.91, 142.61, 142.08, 138.98, N–C_{bridge} 108.19, C_{meso} 102.98, 100.71, 99.68, CH_2 20.28, 19.91, 19.66, 19.57, CH_3 18.20, 18.13, 17.62, 17.40 ppm; UV–vis (CH_2Cl_2) λ_{max} (log ϵ) 396 (4.98), 539 (3.51), 571 (3.60), 615 (3.00) nm. Anal. Calcd for $C_{38}H_{47}N_4O_4Cl$: C, 69.23; H, 7.19; N, 8.50. Found: C, 68.96; H, 7.42; N, 8.42. **7a**: UV–vis (CH_2Cl_2) λ_{max} (log ϵ) 395 (4.86), 536 (3.82), 568 (3.90), 614 (3.51) nm. Anal. Calcd for $C_{42}H_{55}N_4O_4Cl$: C, 70.52; H, 7.75; N, 7.83. Found: C, 70.34; H, 8.05; N, 7.59. **8a**: UV–vis (CH_2Cl_2) λ_{max} (log ϵ) 396 (5.02), 537 (3.87), 568 (3.98), 613 (3.37) nm. Anal. Calcd for $C_{39}H_{49}N_4O_5Cl$: C, 67.96; H, 7.16; N, 8.13. Found: C, 67.83; H, 7.19; N, 7.92. **9a**: UV–vis (CH_2Cl_2) λ_{max} (log ϵ) 398 (5.19), 532 (3.96), 565 (4.11), 612 (3.62) nm. Anal. Calcd for $C_{40}H_{51}N_4O_6Cl$: C, 66.79; H, 7.15; N, 7.79. Found: C, 66.68; H, 7.35; N, 7.53. **10a**: UV–vis (CH_2Cl_2) λ_{max} (log ϵ) 398 (4.99), 536 (3.85), 571 (3.94), 614 (3.45) nm. Anal. Calcd for $C_{44}H_{51}N_4O_4Cl$: C, 71.87; H, 6.99; N, 7.62. Found: C, 71.63; H, 7.24; N, 7.33. **11a**: UV–vis (CH_2Cl_2) λ_{max} (log ϵ) 401 (5.13), 535 (3.94), 569 (4.06), 614 (3.63) nm. Anal. Calcd for $C_{50}H_{55}N_4O_4Cl$: C, 74.01; H, 6.83; N, 6.90. Found: C, 73.85; H, 6.79; N, 6.71. **12a**: UV–vis (CH_2Cl_2) λ_{max} (log ϵ) 408 (5.23), 542 (4.04), 576 (4.19), 622 (3.70) nm. Anal. Calcd for $C_{52}H_{59}N_4O_4Cl$: C, 74.40; H, 7.08; N, 6.67. Found: C, 74.07; H, 7.03; N, 6.46.

(ii) Reaction of Alkynes with the Oxidation Product of (OEP)Co^{II} with $FeCl_3$. (OEP)Co^{II} (100 mg) was treated with $FeCl_3$ (20 equiv) in CH_2Cl_2 (50 mL) for 10 min with vigorous stirring. After this reaction mixture was transferred through a glass filter into another two-necked flask under an argon atmosphere, alkyne (5–10 equiv) was added to the filtrate. The solution was stirred for 4 h at room temperature and then worked up in the same fashion as in (i). **6a**, **9a**, and **11a** were obtained in 78, 78, and 84% yield by using acetylene gas, 2-butyne-1,4-diol, and diphenylacetylene, respectively. If 3 equiv of $FeCl_3$ was used to oxidize (OEP)Co^{II}, the yield of **11a** decreased to 51%.

N^{21},N^{22}-Bridged (OEP)$HFeCl_4$ (6a′,11a′). 6a′: (OEP)Co^{II} was treated with $FeCl_3$ (20 equiv) and acetylene gas according to the above procedure (ii), and then the workup was done similarly without $HClO_4$ treatment to give **6a′** in 80% yield: UV–vis (CH_2Cl_2) λ_{max} 400, 537, 571, 614 nm. Anal. Calcd for $C_{38}H_{47}N_4Cl_4Fe$: C, 60.25; H, 6.25; N, 7.40. Found: C, 60.45; H, 6.31; N, 7.23.

11a′: (OEP)Co^{II}, $FeCl_3$ (5 equiv), and diphenylacetylene were treated according to the above procedure (ii), and then the workup was done similarly without $HClO_4$ treatment to give **11a′** in 72%

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yield: UV-vis (CH_2Cl_2) λ_{max} (log ϵ) 403 (5.14), 537 (3.88), 571 (4.05), 616 (3.58) nm. Anal. Calcd for $C_{50}H_{55}N_4Cl_4Fe$: C, 66.02; H, 6.09; N, 6.16; Fe, 6.14. Found: C, 65.56; H, 5.91; N, 5.99; Fe, 6.78.

[N^{21},N^{22}-(etheno)TPP]$HClO_4$ (6b), [*N*-(β-chlorovinyl)-TPP]Co^{II}SCN (13b), and [*N*-(β-chlorovinyl)TPP]H (14b). (i) Oxidation of (TPP)Co^{II} in the Presence of Acetylene. A CH_2Cl_2 (50 mL) solution of (TPP)Co^{II} (60 mg) was saturated with acetylene gas by bubbling for 1 h under anaerobic conditions. $FeCl_3$ (5.2 equiv) was added at one time. The mixture was vigorously stirred for 1 h at room temperature and then washed with 10% $HClO_4$ and with water twice, successively. Chromatography on silica gel with CH_2Cl_2–acetone (10:1) followed by recrystallization from CH_2Cl_2–hexane afforded **6b** in 66% yield: UV-vis (CH_2Cl_2) λ_{max} (log ϵ) 431 (5.00), 560 (3.97), 600 (3.99), 654 (3.81) nm. Anal. Calcd for $C_{46}H_{31}N_4O_4Cl$: C, 74.74; H, 4.23; N, 7.58. Found: C, 72.58; H, 4.15; N, 7.61.

(ii) Oxidation of (TPP)Co^{II} followed by the Reaction with Acetylene. $FeCl_3$ (4.3 equiv) was added to a CH_2Cl_2 (40 mL) solution of (TPP)Co^{II} (48 mg), and the resulting mixture was stirred for 1.5 h under argon at room temperature to result in the color change to green. Acetylene gas was introduced effectively into this mixture and allowed to react for 3 h. The workup in the same manner as for (i), except that the porphyrin mixture was treated with a saturated NaSCN aqueous solution before chromatographic purification, afforded [*N*-(β-chlorovinyl)-TPP]Co^{II}SCN (**13b**) in 29% yield together with **6b** (47%). **13b**: ^1H NMR (24 °C) 44.1 (×2), 35.8, −2.9 (8 H, pyrrole β-H), 23.3, 19.6, 2.5, −1.8 (8 H, phenyl *o*-H), 13.5, 12.2, 7.4, 7.1 (8 H, phenyl *m*-H), 9.5, 7.6 (4 H, phenyl *p*-H); UV-vis (CH_2Cl_2) λ_{max} (log ϵ) 447 (5.10), 565 (3.94), 616 (4.05), 666 (3.80) nm. Anal. Calcd for $C_{47}H_{30}N_5SClCo$: C, 71.35; H, 3.82; N, 8.85. Found: C, 71.44; H, 3.70; N, 8.44. The yields of **13b** and **6b** varied in this procedure, and [*N*-(β-chlorovinyl)TPP]H (**14b**) was isolated from time to time. **13b** was converted into **14b** with trifluoroacetic acid according to Callot's procedure.[6e] **14b**: UV-vis (CH_2Cl_2) λ_{max} (log ϵ) 433 (5.14), 529 (3.84), 569 (4.00), 617 (3.82), 672 (3.60) nm. Anal. Calcd for $C_{46}H_{31}N_4Cl$: C, 81.82; H, 4.63; N, 8.30. Found: C, 79.97; H, 4.25; N, 8.58.

N^{21},N^{22}-Bridged (TPP)$HClO_4$ (7b–11b). $FeCl_3$ (3.5 equiv) was added at one time to a CH_2Cl_2 (50 mL) solution of (TPP)Co^{II} (100 mg) and alkyne (5 equiv), and the whole mixture was stirred vigorously for 1 h. The workup was done according to the procedure for acetylene described above. Although 1-hexyne, propargyl alcohol, phenylacetylene, and diphenylacetylene could be employed to prepare **7b**, **8b**, **9b**, and **11b** in 47, 67, 45, and 44% yield, respectively, 2-butyne-1,4-diol failed to give the corresponding bridged porphyrin **10b**. When $FeCl_3$ was replaced by $Fe(ClO_4)_3 \cdot 6H_2O$ in this procedure, 2-butyne-1,4-diol and diphenylacetylene afforded **10b** and **11b** in 75 and 90% yields, respectively. **7b**: UV-vis (CH_2Cl_2) λ_{max} (log ϵ) 429 (5.08), 559 (3.88), 594 (4.05), 646 (3.79) nm. Anal. Calcd for $C_{50}H_{39}N_4O_4Cl$: C, 75.51; H, 4.94; N, 7.04. Found: C, 74.16; H, 4.82; N, 6.56. **8b**: UV-vis (CH_2Cl_2) λ_{max} (log ϵ) 429 (5.02), 557 (3.85), 595 (3.99), 647 (3.79) nm. Anal. Calcd for $C_{47}H_{33}N_4O_5Cl$: C, 73.80; H, 4.32; N, 7.28. Found: C, 72.20; H, 4.18; N, 6.79. **9b**: UV-vis (CH_2Cl_2) λ_{max} (log ϵ) 429 (5.09), 554 (3.89), 590 (4.02), 640 (3.73) nm. Anal. Calcd for $C_{48}H_{35}N_4O_6Cl$: C, 72.13; H, 4.41; N, 7.01. Found: C, 70.92; H, 4.28; N, 6.57. **10b**: UV-vis (CH_2Cl_2) λ_{max} (log ϵ) 430 (5.08), 561 (3.88), 596 (4.04), 648 (3.83) nm. Anal. Calcd for $C_{52}H_{35}N_4O_4Cl$: C, 76.60; H, 4.33; N, 6.87. Found: C, 76.78; H, 4.27; N, 6.55. **11b**: UV-vis (CH_2Cl_2) λ_{max} (log ϵ) 432 (5.15), 557 (3.93), 593 (4.10), 641 (3.73) nm.

Reaction of Co(III) Porphyrin π Cation Radicals with Diphenylacetylene. (i) Electrochemical Oxidation. (OEP)Co^{II} (40 mg) in 10 mL of CH_2Cl_2 charged in an H-cell was electrolyzed at +1.2 V (vs Ag/AgCl) with stirring and bubbling argon in the presence of TBAP to generate $[(OEP)^{\bullet +}]Co^{III}(ClO_4)_2$. After the current was stopped, the electrolyzer was turned off and diphenylacetylene (5 equiv) was added to the solution to result in an immediate color change to green. The solution was stirred for 30 min, evaporated, and chromatographed on silica gel with $CHCl_3$ to give **11a**. As the product could not be separated completely from TBAP, the yield (47%) was calculated with the aid of the visible spectral data of the authentic sample.

(ii) Oxidation with Br_2. Br_2 (29 mg) was added to a mixture of (OEP)Co^{II} (100 mg) and CH_2Cl_2 (20 mL). After the whole mixture was stirred for 1 h at room temperature, diphenylacetylene was added.

(iii) Oxidation of (OEP)Co^{III}Cl. Diphenylacetylene (5 equiv) was added to the mixture of (OEP)Co^{III}Cl (60 mg) and $Fe(ClO_4)_3 \cdot 6H_2O$ (ca. 5 equiv) in CH_2Cl_2 (40 mL). The color of the solution changed immediately, and the ordinary workup afforded **11a** in 50% yield.

Acknowledgment. This work was supported by a Grant-in-Aid for Scientific Research on Priority Area from the Ministry of Education, Science, and Culture of Japan, a Grant for Basic Research from the Inamori Foundation of Japan, and a Grant from the Asahi Glass Research Foundation of Japan. We are grateful to Dr. M. Sato (University of Osaka Prefecture) for the measurement of ESR spectra and to Nichigo Acetylene Co. Ltd. (Osaka, Japan) for the gift of extrapure acetylene gas.

Synthetic and Molecular Orbital Study of η^3(3e)-Butadienyl Complexes of Molybdenum

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Received June 22, 1990

Complexes of general formula $MoCl(CO)_2(\eta^3\text{-}CH_2C(CONRR')C{=}CH_2)L_2$ (L_2 = 2,2′-bipyridine, 1,10-phenanthroline) that contain an η^3(3e)-buta-2,3-dienyl ligand are formed by the reaction of Ph_4P-$[MoCl(CO)_3L_2]$ with methanolic 1,4-dichlorobut-2-yne in the presence of primary or secondary amines HNRR′ (R = H, R′ = Me, Et, Pr^n, Ph, $CH_2CH{=}CH_2$, $CH_2C{\equiv}CH$; R = R′ = Me, Et, Pr^n). The perfluorocarboxylate complex $Mo(CO)_2(\eta^3\text{-}CH_2C(CONHMe)C{=}CH_2)$(2,2′-bipyridine)$(O_2CC_3F_7)$ (11), formed by anion exchange, crystallizes in a triclinic space group $P\bar{1}$ with $a = 7.440$ (3) Å, $b = 9.727$ (3) Å, $c = 17.748$ (6) Å, $\alpha = 100.58$ (3)°, $\beta = 94.84$ (2)°, $\gamma = 103.88$ (5)°, $V = 1214.6$ (7) Å^3, and $Z = 2$; $R = 0.064$, $R_w = 0.072$ for 2296 reflections with $I \geq 3\sigma(I)$ having $2 \leq \theta \leq 22°$. An EHMO study of the bonding and potential reactive centers in the ligated η^3-butadienyl ligand is also reported.

Introduction

Factors determining the stereochemistry and reactivity of molybdenum and tungsten(II) complexes of the type $MX(CO)_2(\eta^3\text{-allyl})L_2$ (M = Mo, W, X = halide, and L_2 = bidentate ligand) have been well defined theoretically and experimentally, in order to develop highly regio- and ste-

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