77217-48-2; **4** (R = *t*-Bu), 77217-51-7; **4** (R = allyl), 77217-52-8; **6** (R = Me), 77217-53-9; **6** (R = Et), 77217-54-0; **6** (R = *n*-Pr), 77217-55-1; **6** (R = *i*-Pr), 77217-57-3; **6** (R = *n*-Bu), 77217-56-2; **6** (R = *t*-Bu), 77217-59-5; **6** (R = allyl), 77217-60-8; **8** (R = Et), 88131-26-4; **8** (R = *n*-Pr), 88156-67-6; **8** (R = *i*-Pr), 88131-27-5; **8** (R = *n*-Bu), 88131-28-6; **8** (R = *t*-Bu), 88131-29-7; **9** (R = Et), 88131-32-2; **9** (R = *n*-Pr), 88131-33-3; **9** (R = *i*-Pr), 88131-34-4; **9** (R = *n*-Bu), 88131-35-5; **9** (R = *t*-Bu), 88131-36-6; **9** (R = allyl), 88131-37-7; **10a**, 88131-38-8; **10b**, 88131-39-9; **11a**, 88131-40-2; **11b**, 88131-41-3; **12**, 88131-42-4; **13**, 88131-43-5; **14**, 88131-44-6; **15**, 88131-45-7; **16a**, 88131-46-8; **16b**, 88131-47-9; **17**, 88131-25-3; **18**, 88131-30-0; **19**, 88131-31-1; dicobalt octacarbonyl, 10210-68-1; diphenylacetylene, 501-65-5; hexaphenylbenzene, 992-04-1; phenylacetylene, 536-74-3; 1,2,4-triphenylbenzene, 1165-53-3.

Supplementary Material Available: Appendix I, analysis of the $^{31}P\{^1H\}$ NMR spectra of **16a,b**, tables of ^1H NMR data for complexes **8** and **9** (Table I), ^{31}P NMR data for complexes **8** and **9** (Table II), ^{13}C NMR data for complexes **8** and **9** (Table III), listings of structure factor amplitudes for compounds **17** (Table V), **18** (Table VI), and **19** (Table VII), tables of positional and thermal parameters for compounds **17** (Table VIII), **18** (Table IX), and **19** (Table X), tables of bond distances and angles for compounds **17** (Table XI), **18** (Table XII), and **19** (Table XIII), tables of root mean square amplitudes for compounds **17** (Table XIV), **18** (Table XV), and **19** (Table XVI), and figures of the ^1H decoupled ^{31}P NMR spectra of **16**, R = methyl (Figure 4), and **16**, R = isopropyl (Figure 5) (69 pages). Ordering information is given on any current masthead page.

Reaction of (Octaethylporphyrinato)cobalt Complexes with Diazoacetaldehyde. *N*-(Formylmethyl)- and *N*-(2-Hydroxyethyl)porphyrins

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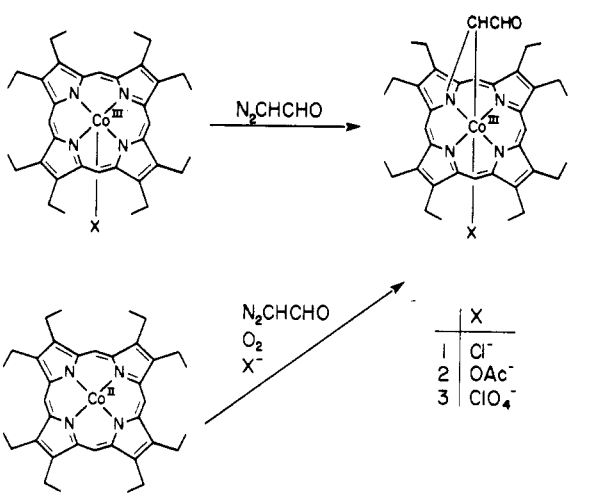
Reaction of divalent and trivalent cobalt complexes of octaethylporphyrin (OEP·H_2) with diazoacetaldehyde gave *N,Co*-(formylmethylene)OEPCo^{III}X (X = Cl^-, OAc^-, ClO_4^-) which were reduced electrochemically to afford *N*-(formylmethyl)OEP·H; *N*-(2,2-dimethoxyethyl)OEP·H and *N,N'*-(1,2-vinylidene)OEP were obtained from *N*-(formylmethyl)OEP·H under acidic conditions. $NaBH_4$ reduction of *N*-(formylmethyl)OEP·H gave *N*-(2-hydroxyethyl)OEP·H. These *N*-alkylporphyrins provide a firm basis for the characterization of some suicide metabolites of cytochrome P-450.

It has recently been reported that cytochrome P-450 monooxygenases are inactivated through the N-alkylation of the prosthetic heme during xenobiotic metabolism and the *N*-alkyl groups may be derived from olefins,[1] acetylenes,[2,3] and 1,4-dihydropyridine derivatives.[4,5] N-Substituted protoporphyrins IX were isolated, as the dimethyl esters, from inactivated cytochrome P-450 enzyme systems and analyzed spectroscopically. However, unequivocal identification of the N substituents has been frustrated due to the difficulties with which authentic materials are synthesized.

N-Alkylporphyrins are prepared by (i) alkylation of free base porphyrins with alkyl halides,[6,7] (ii) metal-to-nitrogen alkyl migration upon one-electron oxidation of (σ-alkyl)-metal(III) porphyrins,[8-11] and (iii) protonolysis of a metal–carbon bond of unusual N,M(III)-bridged methylene complexes of metalloporphyrins.[12-14] The first method

Scheme I



gives reasonably fair yields and selectivity for monoalkylation only when simple alkyl groups such as methyl and ethyl are introduced. Although the second and third methods have allowed N-alkylation to take place under milder reaction conditions, N-alkylation with functionalized alkyl groups is still difficult. There have been no reports on the synthesis of *N*-(2-hydroxyethyl)- or *N*-(formylmethyl)porphyrins which are produced when cytochrome P-450 monooxygenases are inactivated with ethylene or acetylene.[1,2]

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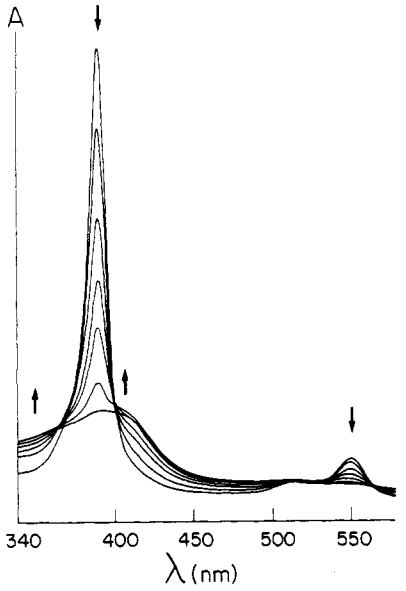


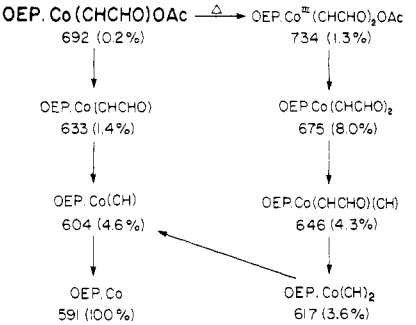
Figure 1. Visible spectral changes during the reaction of $OEPCo^{II}$ with N_2CHCHO in chloroform.

In this work, the reaction of (octaethylporphyrinato)-cobalt complexes (OEPCo) with diazoacetaldehyde to yield the *N,Co*-(formylmethylene)$OEPCo^{III}$ X complexes was studied. These were converted to *N*-(formylmethyl)-OEP·H upon acid treatment after the electrochemical reduction of Co(III) to Co(II). As the only two bridging groups between nitrogen and metal so far known for this type of novel metalloporphyrin are 2,2-diarylvinylidene[12] and ethoxycarbonylmethylene,[13] the formylmethylene-bridging structure has been spectroscopically investigated in detail to reveal the trans effect of the anionic ligand X. In addition, the chemical behavior of *N*-(formylmethyl)-OEP free base and zinc(II) complexes were studied under acidic and basic conditions to yield various N-substituted porphyrins including *N*-(2-hydroxyethyl)OEP·H.

Results and Discussion

When $OEPCo^{II}$ was allowed to react with diazoacetaldehyde[15] in chloroform (Scheme I), the color of the solution turned from red to brown. Monitoring the visible spectrum during the reaction showed a decrease in the intensity of Soret and visible bands. Clean isobestic points suggested that the formation of any 2:1 adduct complexes was negligible[16] (Figure 1). A black precipitate of **1** was obtained by addition of diethyl ether immediately after the disappearance of $OEPCo^{II}$. The ^1H NMR spectrum of **1** shows four singlets at δ 10.21, 9.88, 9.85, and 9.82 due to the meso protons, indicating the low molecular symmetry. Absorptions due to the formylmethylene moiety appeared at δ 3.62 and −1.54 as a pair of AB doublets. This spectrum is consistent with the diamagnetic Co(III) complex formed through the insertion of formylcarbene into a Co–N bond of the cobalt porphyrin with the cobalt being air oxidized to the +3 state and a chloride ligand being derived from the solvent. This parallels the work of Johnson et al., who demonstrated the formation of *N,Co*-(ethoxycarbonylmethylene)$OEPCo^{III}Cl$ through the reaction of ethyl diazoacetate and $OEPCo^{II}$ in chloroform.[13] Although complex **1** was found to be pure enough spectroscopically just after preparation, purification for microanalysis has been frustrated due to its thermal instability. The reaction in the presence of acetic acid afforded a similar compound (**2**) after precipitation with petroleum ether from the reaction mixture. The ^1H NMR spectrum of **2** showed a pair of AB doublets at δ 3.43 and −2.25 along with singlets due to meso protons at δ 10.30, 10.04, and 9.95 (2 H). The mass spectrum of **2** showed the parent ion for (*N,Co*-:CHCHO)$OEPCo^{III}OAc$ at *m/e* 692 with fragment ions at *m/e* 633, 604, and 591 which correspond to the consecutive loss of OAc, CHO, and CH, respectively. Although the disproportionation under the condition of measurement complicates the spectrum as was noted by Johnson et al.,[13] all the additional signals at *m/e* 734, 675, 646, and 617 are interpretable in terms of formation of and fragmentations from $OEPCo^{III}(:CHCHO)_2OAc$ with successive loss of OAc, CHO, and CHO groups, respectively (Scheme II).

Scheme II. Mass Spectrum of (*N,Co*-:CHCHO)$OEPCo^{III}OAc$ (**2**)[a]



[a] Relative intensity of the signals are shown in parentheses.

Table I. ^1H NMR Chemical Shifts of (*N,Co*-:CHCHO)$OEPCo^{III}X$

X	δ ($CDCl_3$) =*CH*CHO	=CHC*H*O	meso-H
Cl^-	−1.54	3.62	9.82, 9.85, 9.88, 10.21
OAc^-	−2.25	3.43	9.95 (2 H), 10.04, 10.30
ClO_4^-	−2.58	3.39	10.18 (2 H), 10.32, 10.59

Trivalent cobalt octaethylporphyrins reacted rapidly with diazoacetaldehyde (Scheme I) since the subsequent oxidation of cobalt was unnecessary. Whereas the formylcarbene adduct from $OEPCo^{III}Br$ turned out to be too labile to obtain a reasonably pure material, the adduct with $OEPCo^{III}(H_2O)_2ClO_4$[17] crystallized out from the reaction mixture upon addition of diethyl ether and was stable enough to allow for full characterization as (*N,Co*-:CHCHO)$OEPCo^{III}ClO_4$ (**3**). Solutions of compound **3**, however, decomposed rapidly. The qualitative trends in the observed thermal lability of the adduct complexes follow the order of trans labilizing effect of the extra ligands: $ClO_4^- < OAc^-$ L Cl^- L Br^-.[18] The chemical shifts data of the adduct complexes **1**, **2**, and **3** are summarized in Table I, showing that the signals due to the formylmethylene group move downfield and at the same time those due to the porphyrin periphery move upfied with increasing trans influence of the anionic ligand X ($Cl^- > OAc^- > ClO_4^-$). This observation is rationalized on the basis of the structural variation caused by the trans in-

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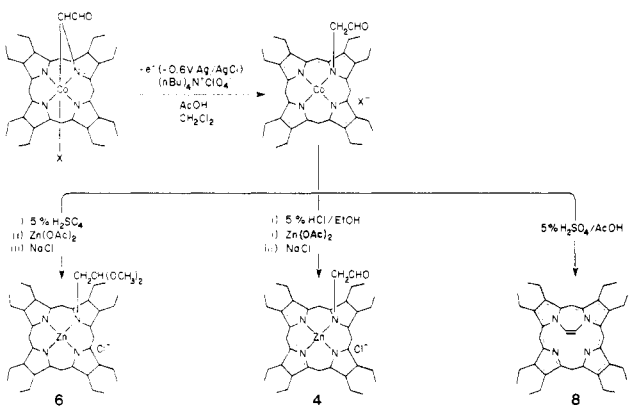
Table II. ^{1}H NMR Data for *N*-Alkyloctaethylporphyrins (δ ($CDCl_3$))[a]

	peripheral			*N*-alkyl		
	meso	CH_2	CH_3	N-C_α(H)	N-C_β(H)	others
4	10.32 (s, 2 H)	3.7-4.3 (m, 16 H)	~1.9 (m, 18 H)	-4.67 (s, 2 H)	6.46 (s, 1 H)	
	10.19 (s, 2 H)		1.67 (t, 6 H)			
5	10.04 (s, 2 H)	3.7-4.2 (m, 16 H)	~1.9 (m, 18 H)	-4.15 (s, 2 H)	6.05 (s, 1 H)	-3.5 (br, 1 H, NH)
	9.93 (s, 2 H)		1.45 (t, 6 H)			
6	10.27 (s, 2 H)	3.7-4.2 (m, 16 H)	~1.9 (m, 18 H)	-5.08 (d, 2 H)	1.40 (t, 1 H)	1.95 (s, 6 H, OMe)
	10.14 (s, 2 H)		1.77 (t, 6 H)			
7	10.03 (s, 2 H)	3.6-4.3 (m, 16 H)	~1.9 (m, 18 H)	-4.89 (d, 2 H)	0.84 (t, 1 H)	1.71 (s, 6 H, OMe)
	9.87 (s, 2 H)		1.49 (t, 6 H)			-3.4 (br, 1 H, NH)
8	10.89 (s, 1 H)	3.8-4.5 (m, 16 H)	1.99 (t, 6 H)	-2.61 (s, 2 H)		
	10.60 (s, 2 H)		1.96 (t, 6 H)			
	10.25 (s, 1 H)		1.84 (t, 6 H)			
			1.78 (t, 6 H)			
9	10.27 (s, 2 H)	3.6-4.4 (m, 16 H)	~1.9 (m, 18 H)	-4.97 (t, 2 H)	0.65 (q, 2 H)	-0.80 (t, 1 H, OH)
	10.14 (s, 2 H)		1.69 (t, 6 H)			
10	10.03 (s, 2 H)	3.4-4.4 (m, 16 H)	~1.9 (m, 18 H)	-4.80 (t, 2 H)	0.10 (t, 2 H)	-1.1 (br, 1 H, OH)
	9.86 (s, 2 H)		1.41 (t, 6 H)			-3.3 (br, 1 H, NH)

[a] **5**, (*N*-$C_\alpha H_2C_\beta HO$)OEP·H; **7**, (*N*-$C_\alpha H_2C_\beta H(OMe)_2$)OEP·H; **8**, (*N*-$C_\alpha H{=}C_\alpha NH$)OEP; **10**, (*N*-$C_\alpha H_2C_\beta H_2OH$)OEP·H; **4**, **6**, and **9** $Zn^{II}Cl$ complex of **5**, **7**, and **10**, respectively.

Scheme III



fluence of X. The observed chemical shift changes above can be related to the ring current change which reflects a sensitivity to the extent of planarity of the porphyrin π system. Since the formylmethylene group is in the shielding region and the porphyrin periphery is the deshielding region, we consider that the smallest ring current effect in the chloride complex **1** is attributed to the greatest tilting of the pyrrole ring, which is involved i the N–C–Co bridge, with respect to the porphyrin plane.[16] The chloride ligand imposes the strongest trans effect resulting in a Co–C bond lengthening which is necessarily accompanied by a widening of the angle between the N–C bond of the N–C–Co bridge and the porphyrin plane.

Controlled electrochemical reduction of the complexes **1**, **2**, and **3**, in the presence of acetic acid proceeded smoothly with a color change from brown to green. Since the reduction product proved to be too unstable to purify, the reaction mixture was treated with acid (Scheme III), immediately after completion of the reduction, in order to remove cobalt ion from the porphyrin, which was finally purified as a zinc complex. Three *N*-alkylporphyrins were isolated depending on the condition of acid treatment for the removal of cobalt. Demetalation with 5% H_2SO_4/MeOH at ambient temperature for 1 h gave a mixture of *N*-(formylmethyl)OEPZnCl (**4**) and the corresponding dimethyl acetal **6** which were separated by preparative TLC. The acetal formation could be avoided by using 5% HCl/EtOH at 0 °C for 30 min; however, its formation was complete in 5% H_2SO_2/MeOH at room temperature for 10 h. *N*-(Formylmethyl)OEPH (**5**) and *N*-(2,2-dimethoxyethyl)OEPH (**7**) were obtained quantitatively by mild acid treatment of the corresponding zinc complexes **4** and **6**. Spin-spin coupling in the *N*-CH_2CHO group was not observed in the ^{1}H NMR spectra of **4** and **5** (Table II), suggesting that a strong interaction of the carbonyl oxygen with zinc(II) in complex **4** and with N–H proton in the complex **5** restricts rotation around the carbon–carbon bond of the *N*-alkyl group. Acid treatment with 5% H_2SO_4/AcOH after the electrochemical reduction gave the N,N-bridged octaethylporphyrin **8** in 22% overall yield from $OEPCo^{II}$. The ^{1}H NMR spectrum of **8** showed three singlets for the meso protons with a 1:2:1 ratio and a singlet (2 H) for the vinyl protons at δ -2.61 ppm. The mass spectrum (*m/e*) 559, M + 1) and the observed inability to bind zinc(II) ion are consistent with the structure in which a 1,2-vinylidene group bridges to adjacent pyrrole nitrogens of OEP. The formation of **8** is explained in terms of acid-catalyzed intramolecular attack of the pyrrole nitrogen on the carbonyl carbon of *N*-(formylmethyl)porphyrin, followed by dehydration. *N,N'-o*-phenylene-bridged protoporphyrin IX dimethyl ester has been isolated from livers of Sprague-Dawley rats treated with 1-aminobenzotriazole,[19] and (*N,N'*-((benzyloxy)methylene)tetraphenylporphyrin-*N''-N'''*)dibromopalladium(II) has also been reported.[20]

Reduction of the formyl group of the zinc complex **4** was readily achieved by using $NaBH_4$ in ethanol to generate *N*-(2-hydroxyethyl)$OEPZn^{II}Cl$ (**9**) in quantitative yield.

During the inactivation of microsomal cytochrome P-450 with acetylene, Ortiz de Montellano et al. extracted a mixture of unseparable *N*-alkylporphyrin IX dimethyl esters, the spectral data of which were difficult to interpret.[3] The present results clearly indicate that their method for esterification of the propionic acid side chain, of the modified heme, with 5% H_2SO_4 in MeOH at 0 °C overnight inevitably causes dimethyl acetalization of the formyl group of *N*-(formylmethyl)porphyrins to give rise to a mixture of *N*-(formylmethyl)- and *N*-(2,2-dimethoxyethyl)porphyrin.

Experimental Section

^{1}H NMR spectra were recorded on Bruker WP-80 and Nicolet H-270 spectrometers using tetramethylsilane as an internal

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standard in $CDCl_3$ solution. Visible spectra were measured in $CHCl_3$ with a Cary Model 17 spectrophotometer. Bulk controlled-potential electrolysis was performed in CH_2Cl_2 at platinum by using a PAR Model 173 potentiostat with an Ag/AgCl couple was a reference. Kieselgel 60F_{254} (Merck) and Silica Gel 60-H (EM Reagents) were used for preparative and column chromatography.

Reaction of OEPCo^{II} with Diazoacetaldehyde. A CH_2Cl_2 solution of diazoacetaldehyde[15] (ca. 10 molar excess) was added to OEPCo^{II} (60 mg) in $CHCl_3$ (25 mL), and the reaction was followed spectrophotometrically. The color of the solution turned brown in 1 h. The solution was concentrated at room temperature, and diethyl ether was added to afford a black precipitate of (*N,Co*-:CHCHO)OEPCo^{III}Cl (**1**). When the above reaction was carried out in the presence of acetic acid (0.1 mL), a precipitate of (*N,Co*-:CHCHO)OEPCo^{III}OAc (**2**) was obtained by using petroleum ether instead of diethyl ether. Visible spectra of **1** and **2** just after the completion of the reaction are virtually the same as that of (*N,Co*-:CHCHO)OEPCo$^{III}ClO_4$ (**3**). The materials **1** and **2** gave reasonable ^1H NMR spectra as shown in Table I; however, satisfactory analytical data were not obtained because all the attempts at purification brought about decomposition.

(*N,Co*-:CHCHO)OEPCo$^{III}ClO_4$ (3). To OEPCo^{III}-$(H_2O)_2ClO_4$[17] (40) mg) dissolved in $CHCl_3$ (5 mL) was added dropwise a CH_2Cl_2 solution of diazoacetaldehyde until the starting material disappeared. The resulting reaction mixture was evaporated to dryness under reduced pressure, and the residue was crystallized from $CHCl_3$ and diethyl ether to give 25 mg of dark brown crystals (**3**) in 62% yield: λ_{max} (log ϵ) 400 (4.68), 502 (3.88), and 574 nm (3.69). Anal. Calcd for $C_{38}H_{46}N_4O_5ClCo\cdot{}^1/_2H_2O$: C, 61.49; H, 6.38; N, 7.55; O, 11.86. Found: C, 61.40; H, 6.39; N, 7.64; O, 11.67.

(*N*-CH$_2$CHO)OEPZn^{II}Cl (4) and (*N*-CH$_2$CHO)OEP·H (5). A 60-mg sample of (*N,Co*-:CHCHO)OEPCo^{III}OAc (**2**) was placed in an H cell, and bulk electrolysis was carried out under argon at −0.6 V in CH_2Cl_2 solution containing 0.1 mL of acetic acid using tetrabutylammonium perchlorate as an electrolyte (ca. 0.1 M). The color of the solution turned from brown to green in 40 min. The solvent was removed under reduced pressure, and the residue was treated with 5% HCl/EtOH in an ice bath for 1 h. The acidic ethanol solution was then partitioned between water and $CHCl_3$. The $CHCl_3$ layer was separated and washed four times with water. The volume of the CHCl3 solution was reduced on a rotary evaporator, after which an equal volume of a MeOH solution containing an excess $Zn(OAc)_2\cdot2H_2O$ was added. This solution was again partitioned between $CHCl_3$ and water. The organic layer was washed with water and three times with saturated NaCl solution, and then dried over anhydrous Na_2SO_4. The solvent was removed, and the residue was chromatographed on silica gel with benzene/acetone (10:1). The green fraction following the first red fraction of OEPCo^{II} was collected, and the green porphyrin was recrystallized from $CHCl_3$ and *n*-hexane to give 32 mg of (*N*-CH_2CHO)OEPZn^{II}Cl (**4**) in 37% overall yield from OEPCo^{II}: Vis λ_{max} (log ϵ) 377 (sh) (4.68), 420 (5.25), 431 (5.20), 536 (4.06), 578 (4.21), and 618 nm (3.64). Anal. Calcd for $C_{38}H_{47}N_4OClZn$: C, 67.45; H, 7.00; N, 8.28. Found: C, 67.06; H, 6.84; N, 8.02.

A 20 mg sample of (*N*-CH_2CHO)OEPZn^{II}Cl (**4**) was dissolved in cold 5% HCl ethanolic solution (10 mL) and allowed to stand for 30 min. This solution was partitioned between $CHCl_3$ and water. The organic layer was washed three times with water, dried over anhydrous Na_2SO_4, and evaporated to give a brown residue which was recrystallized from ethanol. (*N*-CH_2CHO)OEP·H (**5**) was obtained in quantitative yield: Vis λ_{max} (log ϵ) 379 (sh) (4.84), 407 (5.11), 501 (4.12), 531 (3.86), 580 (3.71), and 638 nm (3.54); MS, *m/e* 576 (M). Anal. Calcd for $C_{38}H_{48}N_4O\cdot H_2O$: C, 76.73; H, 8.47; N, 9.42. Found: C, 76.93; H, 8.76; N, 9.13.

(*N*-CH$_2$CH(OCH$_3$)$_2$)OEPZn^{II}Cl (6) and (*N*-CH$_2$CH(OCH$_3$)$_2$)OEP·H (7). The same procedure as described above was used except that acid treatment was carried out with 5% H_2SO_4/MeOH at room temperature for 10 h, instead of 5% HCl/EtOH at 0 °C for 1 h, to give (*N*-$CH_2CH(OCH_3)_2$)OEPZn^{II}Cl (**6**) in 40% overall yield from OEPCo^{II}: Vis λ_{max} (log ϵ) 376 (sh) (4.51), 421 (5.18), 432 (5.11), 538 (3.94), 580 (4.09), and 620 nm (3.55). Anal. Calcd for $C_{40}H_{53}N_4O_2ClZn\cdot{}^1/_2H_2O$: C, 65.66; H, 7.44; N, 7.66. Found: C, 65.49; H, 7.55; N, 7.33.

6 was easily demetalated by using 5% H_2SO_4/MeOH to give (*N*-$CH_2CH(OCH_3)_2$)OEP·H (**7**) in quantitative yield after recrystallization from methanol: Vis λ_{max} (log ϵ) 379 (sh) (4.67), 410 (5.03), 503 (3.99), 535 (3.76), 582 (3.65), and 639 nm (3.40); MS, *m/e* 622 (M). Anal. Calcd for $C_{40}H_5{}_4N_4O_2\cdot{}^1/_2H_2O$: C, 76.03; H, 8.77; N, 8.87. Found: C, 76.37; H, 8.79; N, 8.68.

The solution from above just after electrolysis was treated with 5% H_2SO_4/AcOH for 10 h and then 5% HCl/AcOH for 2 h. The resulting mixture was worked up according to the procedure described above and chromatographed on silica gel with $CHCl_3$/acetone (5:1). The red-brown fraction following the green band of **4** was collected and recrystallized from $CHCl_3$ and *n*-hexane to afford (*N*-CH=CH—N)OEP (**8**) in 22% yield based on OEPCo^{II}: Vis λ_{max} (log ϵ) 393 (5.07), 535 (3.89), 570 (4.00), and 615 nm (3.19); MS *m/e* 559 (M + 1). Anal. Calcd for $C_{38}H_{46}N_4\cdot CHCl_3$: C, 69.07; H, 6.99; N, 8.26. Found: C, 68.71; H, 7.06; N, 8.34.

(*N*-CH$_2$CH$_2$OH)OEPZn^{II}Cl (9) and (*N*-CH$_2$CH$_2$OH)OEP·H (10). To (*N*-CH_2CHO)OEPZn^{II}Cl (**4**) (13 mg) dissolved in ethanol (10 mL) was added $NaBH_4$ (2 mg), and the mixture was stirred for 10 min at room temperature. Saturated NH_4Cl solution (20 mL) was added, and the mixture was extracted into benzene. The organic layer was washed twice with saturated NH_4Cl solution and then twice with water, dried over anhydrous Na_2SO_4, and purified by chromatography on silica gel with benzene acetone (10:1). Recrystallization from $CHCl_3$ and n-hexane gave violet crystals of (*N*-CH_2OH)OEPZn^{II}Cl (**9**) in quantitative yield: Vis λ_{max} (log ϵ) 376 (sh) (4.60), 422 (5.26), 432 (5.19), 538 (4.03), 580 (4.18), and 621 nm (3.63). Anal. Calcd for $C_{38}H_{49}H_4OClZn$: C, 67.25; H, 7.28; N, 8.26. Found: C, 67.02; H. 7.26; N, 8.27.

9 was treated with 5% HCl/MeOH to give (*N*-CH_2CH_2OH)-OEP·H (**10**) in quantitative yield: Vis λ_{max} (log ϵ) 380 (sh) (4.62), 409 (4.95), 503 (3.98), 534 (3.81), 582 (3.73), and 639 nm (3.41); MS, *m/e* 578 (M).

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