ions,[12a] many of which incorporate biologically relevant sulfur-donor ligands), and D^{3+} ($\{HB(Me_2pz)_3\}MoSCl_2$).[12b] These compounds and closely related derivatives provide important benchmark molecules for the development of multiple wavelength X-ray absorption spectroscopy and for the interpretation of X-ray absorption data from enzymes.[3]

The facile conversion of the six-coordinate oxomolybdenum(IV) complexes to their sulfido analogues is the first example of such a reaction for a pseudooctahedral mononuclear molybdenum center. Previous conversions have involved nonoctahedral stereochemistries or polynuclear metal centers.[8-10,29,30]

Finally, we note that the generally broad ^{95}Mo NMR signals for oxomolybdenum(IV) compounds and our inability to observe ^{95}Mo NMR spectra for the sulfidomolybdenum(IV) compounds offer little encouragement for the direct observation of such centers in enzymes by ^{95}Mo NMR.

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Registry No. 1a, 99113-26-5; **1b**, 99127-98-7; **1c**, 99127-99-8; **1d**, 107441-39-4; **2a**, 107441-40-7; **2b**, 107441-41-8; **2b**$\cdot CH_2Cl_2$, 107441-44-1; **2c**, 107441-42-9; **2d**, 107441-43-0; *cis*-$MoO_2(S_2CNMe_2)_2$, 39248-36-7; *cis*-$MoO_2(S_2CNEt_2)_2$, 18078-69-8; *cis*-$MoO_2(S_2CNPr_2)_2$, 18078-70-1; *cis*-$MoO_2(S_2CNBu_2)_2$, 18078-71-2.

Supplementary Material Available: Tables of anisotropic thermal parameters, calculated hydrogen atom positions, and interatom distances and angles for $\{HB(Me_2pz)_3\}MoO(S_2CNEt_2)$ and $\{HB(Me_2pz)_3\}MoS(S_2CNEt_2)\cdot CH_2Cl_2$ (13 pages); structure factor tables for $\{HB(Me_2pz)_3\}MoO(S_2CNEt_2)$ and $\{HB(Me_2pz)_3\}MoS(S_2CNEt_2)\cdot CH_2Cl_2$ (31 pages). Ordering information is given on any current masthead page.

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Synthesis of *N*,*N'*-1,2-Vinylidene and 1,2-Phenylene Bridged Porphyrins. X-ray Crystal and Molecular Structure of an *N*,*N'*-(Diphenyl-1,2-vinylidene)-*meso*-tetraphenylporphyrin

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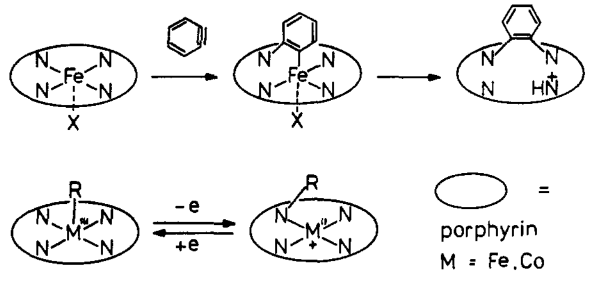
Abstract: The synthesis of *N*,*N'*-1,2-vinylidene and 1,2-phenylene bridged porphyrins, which are models of the inactivation products of cytochrome P-450 in the presence of 1-aminobenzotriazole (ABT) has been accomplished. They are prepared from *N*-aryl- or *N*-styrylporphyrins either by oxidation with amine cation radicals or electrochemically. Alternatively the direct reaction of a cobalt(III) porphyrin with ABT gave an *N*,*N'*-1,2-phenyleneporphyrin and an *N*-phenylporphyrin. The structure of an *N*,*N'*-(diphenyl-1,2-vinylidene)-*meso*-tetraphenylporphyrin, as its hydroperchlorate, was determined by X-ray crystallography. It showed (i) a considerable folding of the new seven-membered ring formed by the introduction of the 1,2-vinylidene group, (ii) that the protonated nitrogen atoms are the unsubstituted ones, and (iii) that the π-electron delocalization in the porphinato core is only moderately affected by the insertion of the two-carbon bridge.

The suicidal inactivation of cytochrome P-450 by 1-aminobenzotriazole (ABT) and related compounds[1,2] is of considerable interest since ABT, by itself of low toxicity, acts as an efficient synergist of insecticides[3] and herbicides[4] by inhibiting the cytochrome P-450 mediated detoxication pathways.

When, in 1981, Ortiz de Montellano and his collaborators[1] suggested structure **1** (4 isomers) as the modified porphyrinic component of deactivated cytochrome P-450, it was the first *N*,*N'*-phenylene bridged porphyrin, and even the first N–C–C–N bridged porphyrin, ever identified or synthesized. Only in 1984, when the full account of the isolation of the natural product was published,[2] appeared simultaneously in the literature[5] the preparation, by acid-catalyzed enamine formation, of an *N*,*N'*-vinylideneporphyrin **2**. This is in contrast with the series of one-carbon-bridged porphyrins which have been synthesized over the last 10 years.[6-8]

Scheme I



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[⊥] I.B.M.C. du C.N.R.S.

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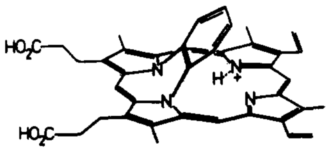
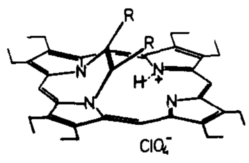


1 (1 of 4 isomers)



2 R = H **3** R = C_6H_5
4 R = alkyl

To explain the natural reaction, an intermediate benzyne (under oxidative conditions ABT acts as an efficient benzyne precursor[9]) was postulated.[2] Its addition across an N–Fe bond followed by Fe → N' migration would lead to the observed products (Scheme I). The metal–nitrogen migration would be one further example of a now classical reaction of organometalloporphyrins[10-11] (Scheme I).

In the present article[12] we will describe several methods for obtaining two-carbon bridged porphyrins, either by forming successively two N–C bonds or by a one step biomimetical bridging reaction. In particular the first synthesis of *N,N'*-1,2-phenyleneporphyrins and the first crystal structure of a *N,N'*-1,2-vinylideneporphyrin will be presented. While this work was completed, an elegant and conceptually different synthesis of *N,N'*-1,2-vinylideneporphyrins **3** was published by Setsune and et al.[13] starting from a cobalt porphyrin cation radical and an alkyne as a model for a hypothetical benzyne intermediate.

Preparative Results and Discussion

Cyclization of Cobalt(II) *N*-Styrylporphyrins. Styrylcobalt(III) porphyrins **5** and **6** (*meso*-tetraphenylporphyrin series = TPP) were obtained from halogenocobalt(III) porphyrins and diazo esters according to known procedures.[14] To avoid the loss of cobalt and the deactivation of the porphyrin nucleus on protonation, we performed the migration step **5** and **6** → **7** and **8**, respectively, by using $(p\text{-BrC}_6H_4)_3N^{\bullet+}SbCl_6^-$ (**9**) instead of the usual acidic conditions (CF_3COOH/air).[11b,c] It was not necessary to isolate compounds **7** and **8**, and, in the presence of an excess oxidant, we directly obtained the $SbCl_5$ complexes **10** (20%) and **11** (12%).

The very low polarity of **10** and **11** excluded a saltlike structure as $(H\text{-porphyrin})^+\text{-}SbCl_6^-$. Analytical data confirmed that a neutral porphyrin–$SbCl_5$ was present (another neutral porphyrin–$SbCl_5$ complex will be described later in this article). In these compounds the porphyrin acts as a neutral monodentate ligand whereas in all known antimony–porphyrin complexes characterized so far the macrocycle acts as a tetradentate ligand[15] (Scheme II).

The $SbCl_5$ complexes are rather unstable in solution and were always accompanied by a polar fraction formulated as the corresponding salts **12** (9%) and **13** (26%) which were isolated as perchlorates. The conversion could be quantitatively performed when a CH_2Cl_2 or toluene solution of **10** or **11** was treated with HCl or silica gel (this last reaction is slow enough at room temperature to allow the isolation of pure **10** and **11**). Salts **12** and **13** were also prepared direclty from **5** and **6** by using the cation radical $(p\text{-BrC}_6H_4)_3N^{\bullet+}ClO_4^-$ (**14**). The rather low total yields (**10** + **12**: 29% and **11** + **13**: 38%) reflect the low yields in the styrylcobalt → cobalt *N*-styrylporphyrin step. When compound **7** was isolated and treated with **14** it gave **12** in 68% yield. The bridging reaction was extended to the octaethylporphyrin series (OEP), and **15** gave **16** on treatment with excess **14**.

The visible and NMR spectra of the bridged porphyrins, as $SbCl_5$ complexes or as salts, are almost identical suggesting that $SbCl_5$ and the proton are located on the same N atom(s) and exert a similar effect on the macrocycle. Both the $SbCl_5$ complexes and the salts display the expected high field resonances for the bridge protons, e.g., methyl signal at −2.99 ppm for **10** and **12**. The bridge ortho phenyl proton resonances at 0.65 ("inside") and 4.35 ppm ("outside") illustrate for **10** and **12** the very large chemical shift differences induced by the relative positions of these protons with respect to the porphyrin π-system. The spectra of **11** and **13** gave two additional informations: (a) The signals of the pyrrole protons (2 AB systems) indicate a plane of symmetry, at least above −50 °C; the $SbCl_5$ group or the proton attached to N must exchange rapidly from one N opposite to the bridge to the other. The location of the proton was confirmed by X-ray structure determination (see below) while the structure of the known $PdBr_2$ complex of a one-carbon bridged porphyrin[7] strongly suggested, by analogy, that $SbCl_5$ should be attached to the same N atoms. (b) At 25 °C a very broad signal at ca. 2.6 ppm could only be attributed to the ortho protons of the bridge phenyl groups. Variable temperature ^1H NMR allowed us to determine a 11.5-kcal activation barrier corresponding to the restricted rotation of the two phenyl groups (at −20 °C). Two broad signals at ca. 1 and 4.1 ppm were present at −50 °C (in good agreement with the NMR data for **12**; insolubility limited the investigations at lower temperatures).

Before we were able to obtain monocrystals of a bridged porphyrin and an X-ray structure determination, there remained an alternative between two isomeric structures A (two-carbon bridge) or B (one-carbon bridge). A compound of type B, **17**, was described by Mansuy and others,[8] and its spectral data were not different enough to convince us that we were handling a different series of bridged macrocycles. However, although both series show the same elements of symmetry, a very useful indication was expected from ^{13}C NMR measurements: depending on the structure, A or B, the vinylidene carbons should give one or two signals. To enhance the bridge carbons signal(s) we prepared **11** by using ^{13}C enriched starting materials (see the details of the synthesis in the Experimental Section).

The ^{13}C NMR spectra were run in $CDCl_3$ and CD_3COCD_3 at 200 MHz under conditions (J modulated spin-echo, delay $^1/_2$ J) suitable to observe selectively the quaternary carbons. Only one peak at 124.40 ($CDCl_3$) or 125.0 ppm (CD_3COCD_3) showed a signal enhancement in the spectrum of the labeled compound. All other resonances corresponding to quaternary carbons were well resolved and clearly identified. This supported the structural assignments which were later confirmed by an X-ray structure determination of compound **13** (see below).

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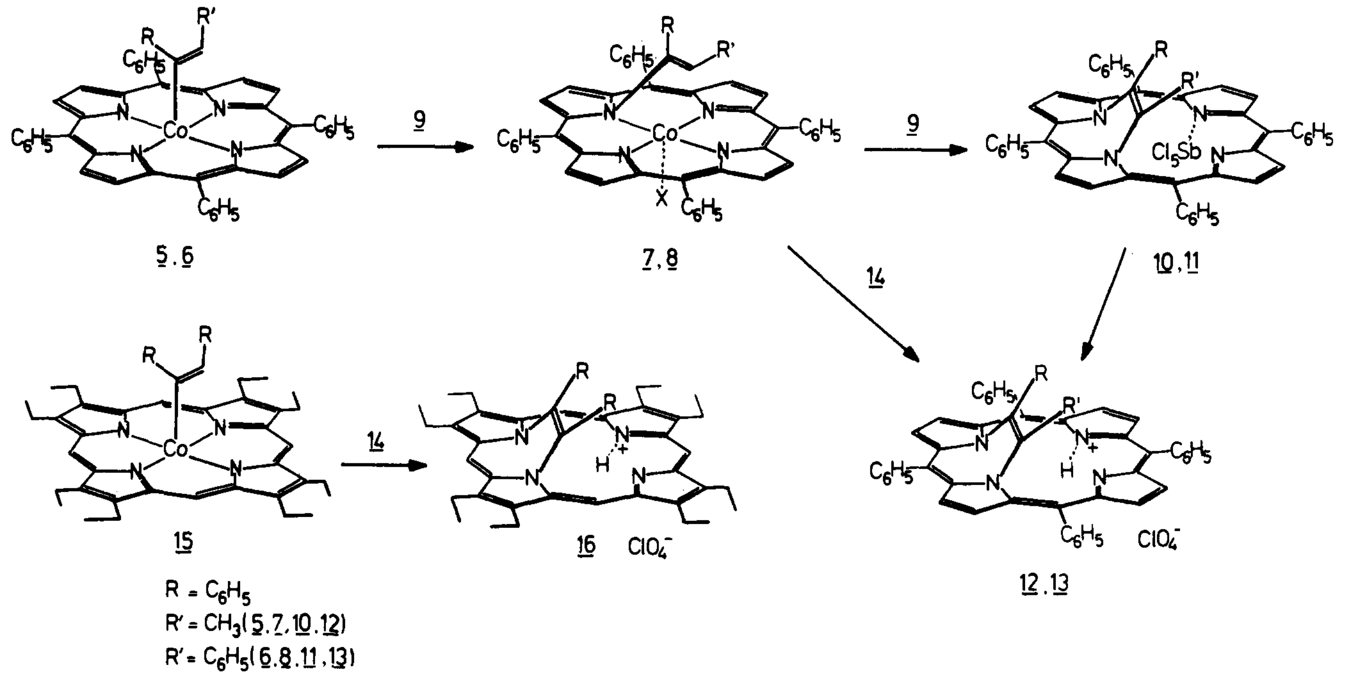
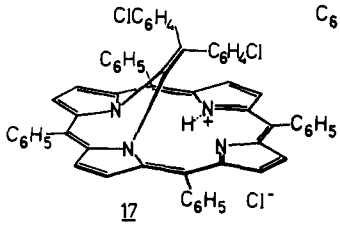
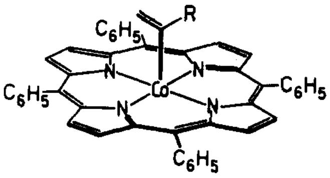
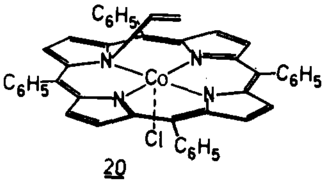
Scheme II



We tried to extend the bridging reaction to less substituted substrates like the cobalt complexes of simple *N*-styryl- or *N*-vinyl-*meso*-tetraphenylporphyrins. Compound **18** was already known in the literature[11c] while vinylcobalt(III) *meso*-tetraphenylporphyrin **19** was obtained from $[\mathrm{Co^{I}TPP}]^-$ and acetylene. Acid-catalyzed rearrangement of **19** gave **20** after metalation. However, treatment of **18**, **19**, or **20** with **9** never gave a trace of a bridged porphyrin.


17


18 R = H 19 R = p-tolyl


20

Preparation of *N*,*N*′-1,2-Phenyleneporphyrins. Two methods allowed us to obtain bridging phenylene groups from mono-N-substituted porphyrins: either an olefinic substrate is oxidatively cyclized to a product which can, in a subsequent step, be aromatized, or an *N*-arylporphyrin is directly cyclized to the desired structure. The first attemps using the second—and more elegant—method being unsuccessful, we prepared the N-substituted porphyrin **22** (27%) from the known **21**,[14b] and oxidized it at low temperature to **23** (at temperatures above 0 °C extensive decomposition occurred) (Scheme III). Dehydrogenation of **23** (DDQ) gave *N*,*N*′-1,2-naphthyleneporphyrin **24** (56%). Again the high field signals of the aromatic bridge protons confirmed the proximity of the π-system (naphthylene H-3 at 2.18 ppm). Having in hand a method for building an aromatic bridge we chose OEP which is a closer model of the natural products and followed the same reaction sequence. Unfortunately the dehydrogenation of **25** gave a highly insoluble solid which could not be characterized.

As said above the first attempts toward the direct cyclization failed. Chlorocobalt(II) *N*-(*p*-methoxyphenyl)-*meso*-tetraphenylporphyrin **30** or its precursor **27** were treated with **9**: no bridged compound was observed but instead the slow formation of a product of low polarity which was characterized as **32** (similar results were obtained in the phenyl and 3,4-dimethoxyphenyl series but will not be described here). **32** was independently prepared from the free base **35** and $\mathrm{SbCl_5}$. The NMR data for **32** indicate a plane of symmetry: either $\mathrm{SbCl_5}$ or H is attached to pyrrole C (A being arylated), the remaining group exchanging rapidly, on the NMR time scale, between pyrroles B and D (Scheme IV).

A successful cyclization of an aryl group was only achieved after two modifications of the procedure: replacement of **9** by **14** to avoid the "freezing" of the reaction by demetalation followed by $\mathrm{SbCl_5}$ complexation and application of heat. A first attempt using **31** in refluxing 1,2-dichloroethane (the methoxy groups were placed to activate the aromatic fragment and end with a symmetrical product) gave **34** (38%; not optimized). Extension to the phenyl series required a prolonged reflux in *sym*-tetrachloroethane, and **33** was obtained in good yield (66%). Demetalation of the cobalt *N*-arylporphyrins is a general side reaction. As a result it is rather difficult to separate the bridged porphyrin from the mono-N-substituted base, both being protonated on silica gel. This was overcome by treating the crude mixture with cobalt acetate: only the *N*-arylporphyrin was metalated, and the less polar complex (= starting material + metalated base) could be easily separated from the bridged salt. The same reaction, when applied to the OEP series, failed under chemical conditions (see below for an electrochemical synthesis). Both **33** and **34** show typical NMR spectra for a bridged structure: high field signal for the protons ortho to the pyrrolic N (2.37 and 1.81 ppm, respectively) and an apparent plane of symmetry which reflects a rapid proton exchange between the unsubstituted N atoms.

In the case of the *N*-phenyl- → *N*,*N*′-phenylene-*meso*-tetraphenylporphyrin cyclization we wondered whether cobalt could be replaced by other metals, and accordingly the cyclization conditions were applied to the corresponding $\mathrm{Cu^{II}}$-, $\mathrm{Zn^{II}}$-, $\mathrm{Fe^{II}}$-, $\mathrm{Ni^{II}}$-, and $\mathrm{Mn^{II}}$-*N*-PhTPP's **36**–**40** and also to the free base *N*-PhTPP **41**, but only in the case of manganese did we isolate **33** albeit in low yield (10%). Compounds **36**, **37**, and **38** decomposed or demetalated whereas **39** suffered from both loss of metal and phenyl group to end as a mixture of **41** and NiTPP. Base **41** survived the reaction conditions.

Electrochemical Experiments. In order to analyze the oxidation step and, hopefully, to optimize the reaction conditions, we replaced cation radicals **9** and **14** by anodic oxidation. The cobalt(II) N-substituted porphyrins exhibited two monoelectronic oxidation

Scheme III

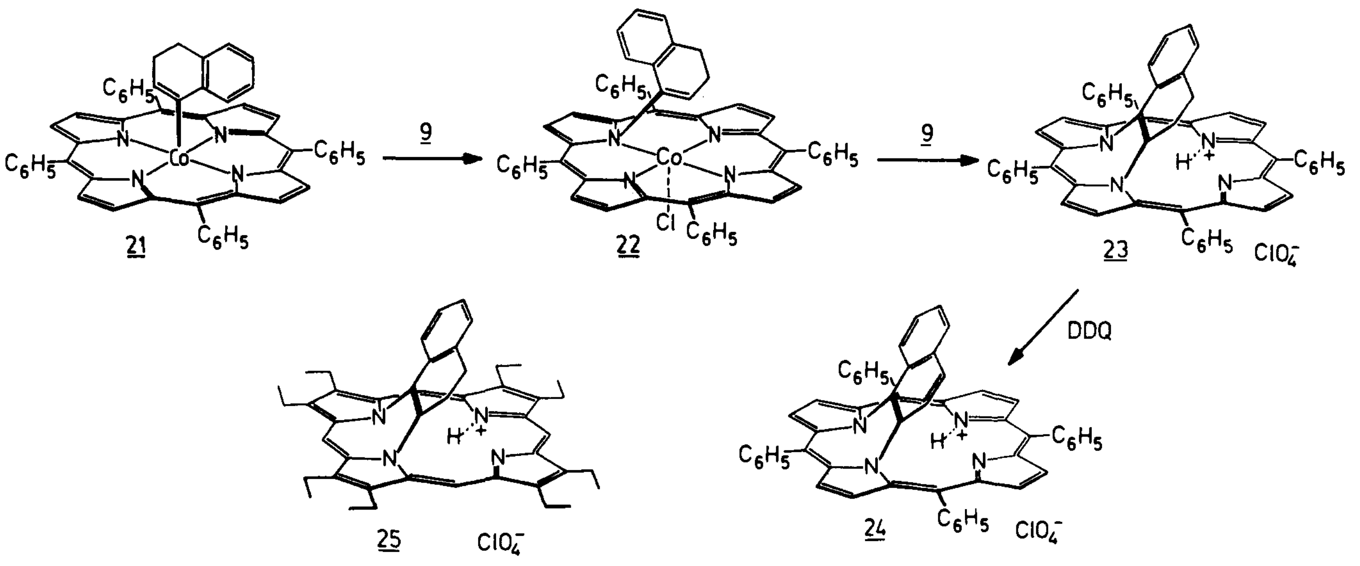


Table I

starting material	$E_{1/2}^{ox}$,[a] V/SCE ± 0.01 V 1st wave	 2nd wave	preparative electrolyses potential[b]	 time (h)	 T (°C)	 yield[c] (%)
7	0.88	1.58	1.10	2	25	57
29	0.93	1.54	1.30	6	120	7
31	0.91	1.54	1.30	2	60	32
42	0.80	1.10	0.85	74	120	3

[a] Half-wave potentials (vs. SCE ± 0.01 V) on a Pt RDE (1000 rev × min^{-1}) in 1,1,2,2-tetrachloroethane (1,2-dichloroethane for 7) + n-$Pr_4N^+ClO_4^-$ (0.05 M). [b] Same conditions as *a* but stationary electrode. [c] Bridged porphyrins only.

Table II

compd	$E_{1/2}^{ox}$ ± 0.01 V[a,b] 1st wave	 2nd wave	ΔE[c]
36	1.25	1.77	0.52
37	1.13	1.59	0.46
38	0.45	1.60	1.15
40	0.71	1.54	0.83
29	0.93	1.54	0.61
41	0.72	1.17	0.45

[a] Same conditions as indicated in Table I. [b] Nickel complex **39** was not studied due to its decomposition. [c] $\Delta E = E_{1/2}^{ox}$ (1st wave) − $E_{1/2}^{ox}$ (2nd wave).

waves (see Table I). The first wave is diffusion controlled and almost reversible. Analysis of the cyclic voltammetry data (relations between v and I_{pa}, I_{pa}/I_{pc}, E_{pa}) showed that the first oxidation wave was followed by a slow chemical reaction confirming that the electrochemical synthesis of bridged porphyrins was feasible. The half-wave potentials fell within a narrow range (TPP series) and were more positive by ca. 0.25 V than that of the "normal" porphyrin CoTPP.

The preparative electrolyses were run at potentials intermediate between the first and the second oxidation waves on the diffusion plateau of the first wave. The supporting electrolyte had to be soluble in the rather nonpolar chlorinated solvents but at the same time had to be hydrophilic enough to be eliminated at the end of the reaction by water washings. We chose n-$Pr_4N^+ClO_4^-$ rather than the more widely used $Et_4N^+ClO_4^-$ (insoluble in chlorinated solvents) or n-$Bu_4N^+ClO_4^-$ (too lipophilic to be extracted). As in the above described chemical reactions heat had to be applied to cyclize the aromatic groups.

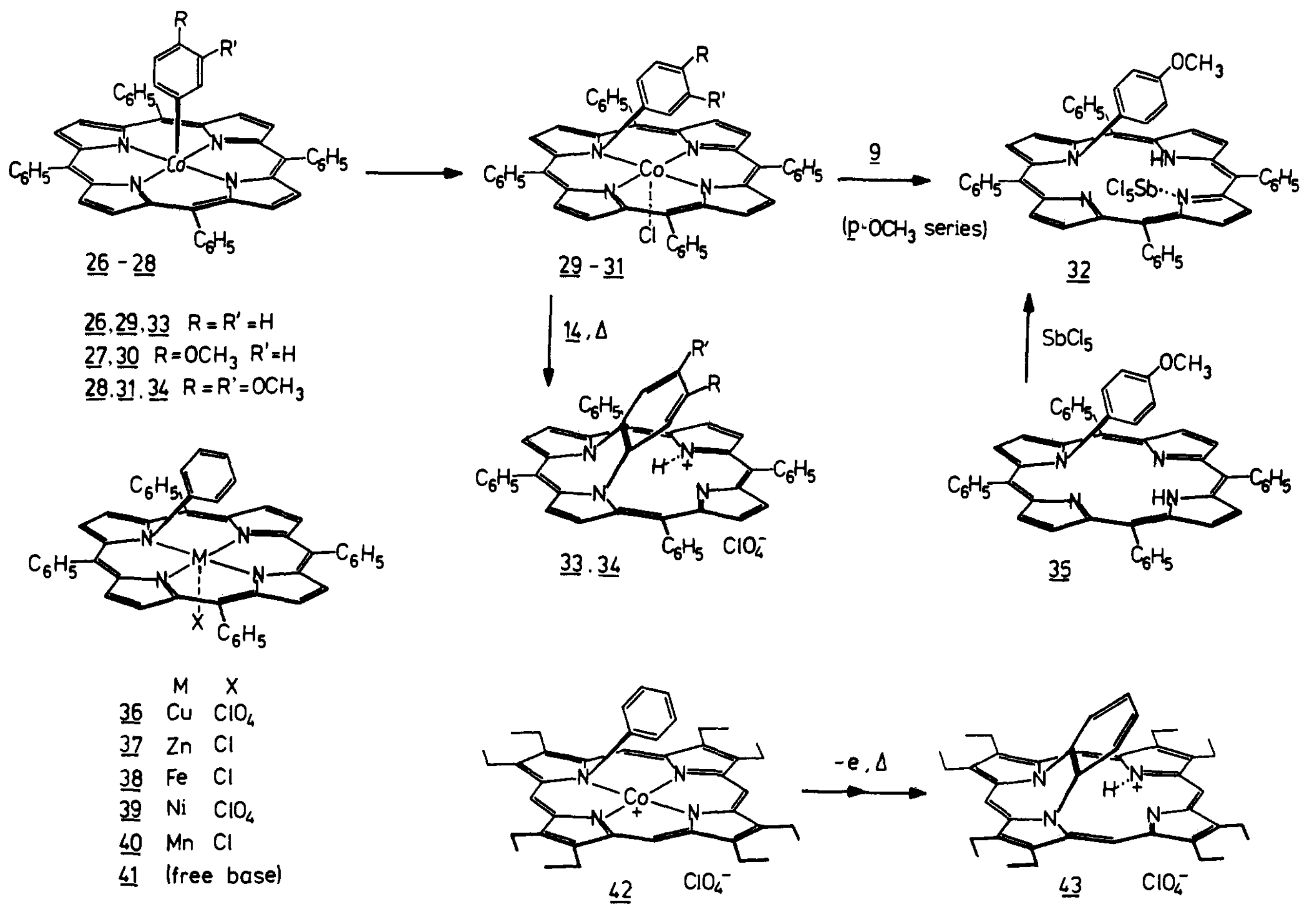
Two significant differences between the results obtained under chemical and electrochemical conditions were noted: (a) the demetalation of the starting cobalt complexes is amplified during anodic oxidation and severely limits the yields, in particular at high temperatures; (b) whereas an OEP bridged by an aryl group could never be prepared under purely chemical conditions, the use of drastic electrochemical + thermal conditions allowed the isolation of **43** (3%) which is the closest model of the natural product. Half-wave potentials were also measured for compounds **36–38** and **40** (see Table II) under the same conditions as for the cobalt complexes. Data for **29** (cobalt) and **41** (free base) were added for comparison. The large differences observed for the first wave are not reflected in the $E_{1/2}^{ox}$ of the second wave, a parallel behavior being observed for **36**, **37**, and the free base **41** while large fluctuations of the first wave with regard to the second occurred for **38**, **40**, and **29**.

Direct Preparation of an *N,N'*-1,2-Phenylene Porphyrin from ABT and a Cobalt(III) Porphyrin. We earlier found[11c] that a model reaction of the oxidation of hydrazines by natural systems, like the active Fe–O form of cytochrome P-450, could be performed: not only cobalt(III) porphyrins oxidize arylhydrazines but the products—arylcobalt(III) porphyrins—are analogues of the aryliron(III) porphyrins, primary products of the inhibition of cytochrome P-450. ABT being a hydrazine derivative we thought that the direct reaction of ABT with a cobalt(III) porphyrin might produce an *N,N'*-1,2-phenyleneporphyrin. Indeed, on prolonged heating (>90 °C; no reaction occurred at lower temperatures) and after the usual isolation procedure (see Experimental Section) we obtained two products **33** (16%) and **29** (29%) from $ClCo^{III}TPP$ and ABT. In addition to **33** and **29** some free base **41** could be detected in the crude reaction mixture, but to facilitate the isolation of the products it was metalated to **29**. We checked that **33** and **29** did not interconvert under the reaction conditions (Scheme V).

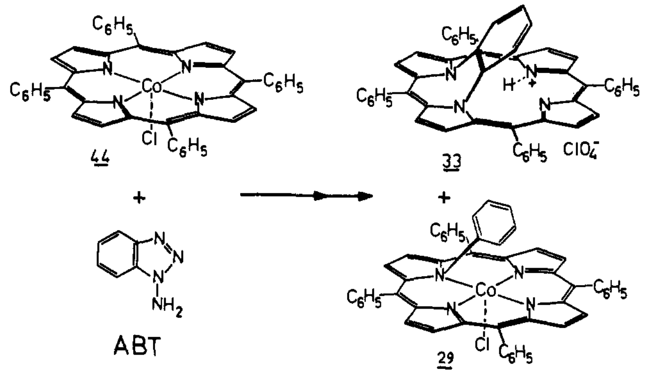
To test Ortiz de Montellano's hypothesis[2]—the oxidation of ABT gives benzyne which then reacts with the metalloporphyrin—we ran our reaction in the presence of tetraphenylcyclopentadienone, which is known to trap efficiently benzyne as tetraphenylnaphthalene (TPN).[9b] No TPN could be detected in addition to **33** and **29**, but instead several colorless products corresponding to the addition of ABT to the ketone were isolated but not fully characterized. The same side products were found in a blank experiment in the absence of cobalt(III) porphyrin.

Discussion. The bridge formation from cobalt(II) *N*-styryl- or *N*-arylporphyrins is obviously a multistep process (Scheme VI, *N*-phenyl series). The first reaction is a one-electron oxidation (as measured by coulometry) for which three sites are available: cobalt, porphyrin π-system, or the organic group attached to N. This last group, due to the geometry of the molecule, is not conjugated to the porphyrin π-system to which it is almost perpendicular.[16] It can be immediately excluded as an oxidation

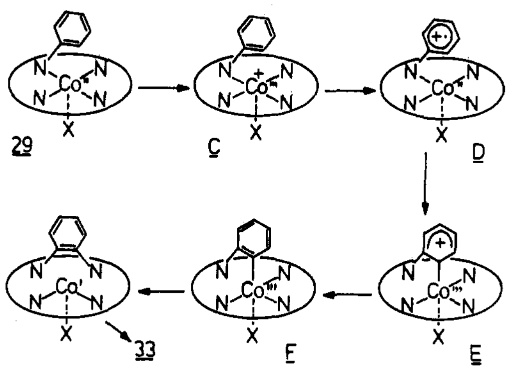
Scheme IV



Scheme V



Scheme VI



site: one would expect large differences of the $E_{1/2}$ as a function of the substitution (phenyl/dimethoxyphenyl for example). As shown in Table I this was not observed. A choice between the remaining oxidation sites could be made after quantitative electrolysis of **29** little above the first oxidation wave. The ESR signal due to the paramagnetic cobalt(II) disappeared thus suggesting that the product was a diamagnetic cationic cobalt(III)[17] species C (electrolysis above the second oxidation wave led to the slow increase of an ESR signal attributed to a π-cation radical). In a second step an electron transfer[18] from an aryl (or a styryl) group to the metal would give an organic cation radical D (*N*-phenyl series). This step would obviously be facilitated by electron-donating groups or the delocalization of the created charge. The easier transformation of more substituted phenyl or styryl groups confirmed this interpretation.

At this stage we earlier proposed[12a] a nucleophilic attack by a vicinal pyrrolic N, such a process recalling the known anodic oxidative functionalization of aromatics.[19] We now favor a Co–C bond formation by radical recombination to form E. Rearomatization by loss of a proton would then give F. Although such a structure (two atoms inserted between the metal and a pyrrolic

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[16] This is typical for ClZn(*N*-Ph)TPP which can be considered as a good model for the corresponding cobalt complexes. See: Kuila, D.; Lavallee, D. K.; Schauer, C. K.; Anderson, O. P. *J. Am. Chem. Soc.* **1984**, *106*, 448–450.

[17] Recently Chang et al. (Salehi, A.; Oertling, W. A.; Babcock, G. T.; Chang, C. K. *J. Am. Chem. Soc.* **1986**, *108*, 5630–5631) showed evidence, in the OEP series, for an ESR silent cobalt(II) porphyrin π-cation radical. However in the presence of chloride instead of perchlorate counterion we think that an equilibrium, if any, may be in favor of a metal-centered cation. In addition the absence of bridge formation from the π-cation radicals of the Cu and Zn analogues strongly suggests a direct involvement of the metal in the electron-transfer step.

[18] (a) Kochi, J. K. *Organometallic Mechanisms and Catalysis*; Academic Press: New York, 1978; Chapter 5. (b) Sheldon, R. A.; Kochi, J. K. *Metal Catalyzed Oxidation of Organic Compounds*; Academic Press: New York, 1981. (c) Morimoto, T.; Hirano, M.; Echigoya, K.; Sato, T. *J. Chem. Soc., Perkin Trans. 2* **1986**, 1205–1209, and references cited therein.

[19] Ross, S. D.; Finkelstein, M.; Rudd, E. J. *Anodic Oxidation*; Academic Press: New York, 1975; pp 82–99.

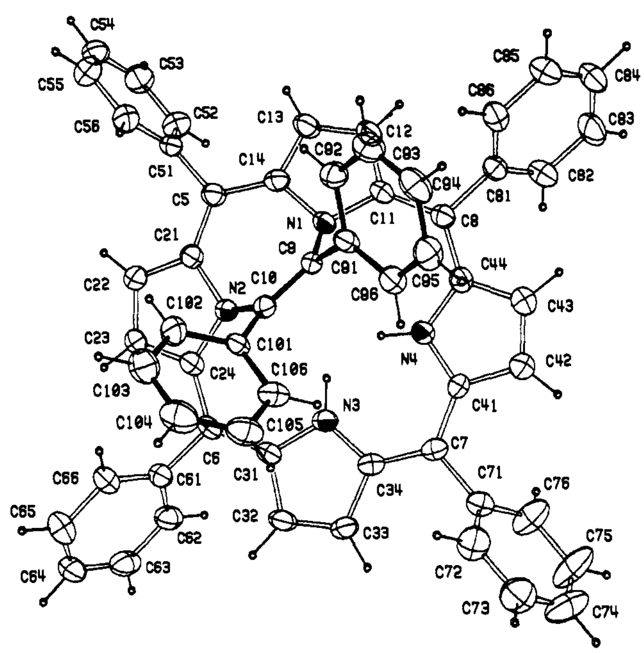

Figure 1. An ORTEP drawing of **13** showing the atom labeling scheme.

N) has not yet been characterized, it has been suggested by Ortiz de Montellano[2] as a possible intermediate in the course of the natural reaction. One should also remember that compounds in which one[20] or three[21] atoms are inserted have been synthesized. A reductive elimination from F, similar to that which results in Co → N migrations, will give the bridged structure. Loss of cobalt could then be followed, in the presence of **9** and under the mild conditions used for cyclizing the styryl groups, by the formation of the $SbCl_5$ complex.

The results obtained with metal complexes **36–38** and **40** can be rationalized if one considers the corresponding redox potentials and oxidation sites. Only in the case of **38** and **40** (Fe, Mn) is a higher oxidation state of the metal easily accessible. However only for **40**[22] is the resulting species a strong enough oxidant to carry out the subsequent electron transfer ($E_{1/2}$ = 0.71 vs. 0.45 V for **38**). For **36** and **37** (Cu, Zn) the oxidation site is the porphyrin π-system, and the electron transfer to the π-cation radical is inefficient enough to allow the omnipresent side reaction, loss of metal, to operate. The reaction which is limited to the nickel complex, cleavage of the phenyl–nitrogen bond, illustrates the great tendency of nickel to prefer a square planar environment.

The direct reaction, ABT + $ClCo^{III}TPP$, involves first the oxidation of ABT, which is probably coordinated to the metal. In the view of recent findings,[23] about the behavior of ClCoTPP when it is heated in chlorinated solvents, the oxidizing species could be either cobalt(III), the corresponding π-cation radical, or Cl$^\bullet$. The oxidation will be followed by trapping of the resulting benzyne by the cobalt porphyrin to give intermediate F, which then suffers a reductive elimination to the bridge structure or a protonation to a *N*-phenylporphyrin (this last possibility may also occur in the *N*-aryl/styryl cyclization reaction but cannot be evaluated since it will rebuild the carbon skeleton of the starting material). As the reaction proceeds any cobalt(II) formed can be reoxidized to cobalt(III) by dioxygen. The fact that no benzyne could be trapped, at least within the limits of detection of TPN, suggests that it reacts as it is formed but also leaves open the possibility of mechanisms not involving benzyne.

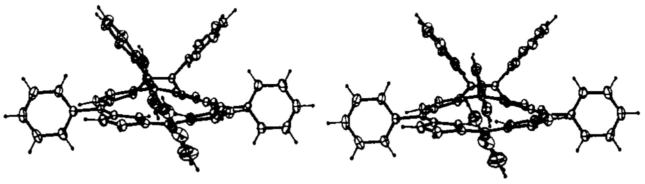

Figure 2. Stereoscopic view of **13**.

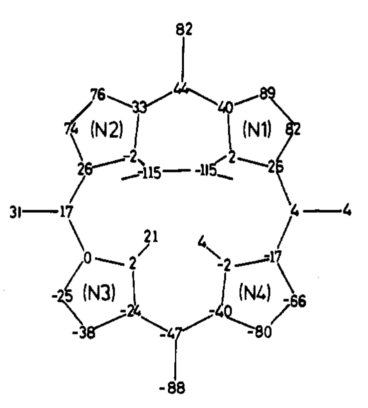

Figure 3. The deviations of atoms (Å × 10^2) from the mean plane (4N). The orientation is as in Figure 1; negative values for atoms which are above the mean plane.

Crystal Structure of 13. The protonated nonmetallo *N,N'*-(diphenyl-1,2-vinylidene)porphyrin is shown in Figure 1 with the atomic labeling scheme. The 1,2-vinylidene group bridges two adjacent nitrogen atoms N1 and N2. The single hydrogen atom on a nitrogen of this protonated species is represented by the two observed and supposed half-occupied positions, as was strongly indicated by two-electron density peaks in the vicinity of N3 and N4. They are noted HN3 and HN4, whereas the remaining hydrogen atoms are noted Hn, Hn being bonded to Cn. The presence of the proton on N3 or N4 can be confirmed by indirect means, since several bond angles in the porphyrin skeleton have been shown to be very sensitive to imino vs. amino nitrogen atoms.[24,25] For example the C_α–N–Cα and N–C_α–C_β angle values lie between the corresponding average values for imino and amino nitrogen atoms.[26] Thus the bridge nitrogen atoms are not protonated. Accordingly, Setsune's formula[13] should be modified as shown in **3**.

The four pyrrole nitrogen atoms are approximately coplanar. The plane so defined is noted (4N). As is normally found the four individual pyrrole rings are planar. A table with the characteristics of all mentioned planes is deposited as Supplementary Material.[42] The vinylidene bridge forces the substituted pyrrole rings (N1) and (N2) to be highly canted from the mean plane (4N), by 22.9 and 20.6° respectively. The two protonated (or better half-time protonated) pyrrole rings (N3) and (N4) are tilted in the direction opposite to that of the N-substituted rings (N1)

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(20) (a) Batten, P.; Hamilton, A. L.; Johnson, A. W.; Mahendran, M.; Ward, D.; King, T. J. *J. Chem. Soc., Perkin Trans. 1* **1977**, 1623–1628. (b) Callot, H. J.; Tschamber, T.; Chevrier, B.; Weiss, R. *Angew. Chem.* **1975**, *87*, 545–546. (c) Chevrier, B.; Weiss, R. *J. Am. Chem. Soc.* **1976**, *98*, 2985–2990. (d) Callot, H. J.; Chevrier, B.; Weiss, R. *J. Am. Chem. Soc.* **1978**, *100*, 4733–4741. (e) Ichimura, K. *Bull. Chem. Soc. Jpn.* **1978**, *51*, 1444–1449. (f) Callot, H. J.; Schaeffer, E. *Nouv. J. Chim.* **1980**, *4*, 307–310. (g) Chevrier, B.; Weiss, R.; Lange, M.; Chottard, J.-C.; Mansuy, D. *J. Am. Chem. Soc.* **1981**, *103*, 2899–2901. (h) Goff, H. M.; Philippi, M. A. *Inorg. Nucl. Chem. Lett.* **1981**, *17*, 239–242. (i) Olmstead, M. M.; Cheng, R. J.; Balch, A. L. *Inorg. Chem.* **1982**, *21*, 4143–4148. (j) Balch, A. L.; Chan, Y.-W.; Olmstead, M. M. *J. Am. Chem. Soc.* **1985**, *107*, 6510–6514.

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(22) Although the Fe(II)/Fe(III) redox potential is shifted toward more positive values after substitution of a pyrrolic nitrogen, the extent of the shift is not sufficient. For $E_{1/2}$ measurements on complexes of N-substituted porphyrins see, also: (a) Lavallee, D. K.; Bain, M. J. *Inorg. Chem.* **1976**, *15*, 2090–2093. (b) Anderson, O. B.; Kopelove, A. B.; Lavallee, D. K. *Inorg. Chem.* **1980**, *19*, 2101–2107. (c) Kuila, D.; Kopelove, A. B.; Lavallee, D. K. *Inorg. Chem.* **1985**, *24*, 1443–1446.

(23) Kohno, M. *Bull. Chem. Soc. Jpn.* **1986**, *59*, 2053–2061, and references cited therein.

(24) Butcher, R. J.; Jameson, G. B.; Storm, C. B. *J. Am. Chem. Soc.* **1985**, *107*, 2978–2980.

(25) Jameson, G. B.; Ibers, J. A. *J. Am. Chem. Soc.* **1980**, *102*, 2823–2831.

(26) The subscripts α, β, *m*, and *p* refer to the α and β carbons of a pyrrole ring, the meso methine carbon atoms, and the phenyl carbon atoms bonded to the core, respectively.

Table III. Selected Bond Distances (Å) and Bond Angles (deg)[a]

(a) Bond Distances

N1–C11	1.403 (7)	C31–C6	1.405 (9)	C6–C61	1.494 (7)	C83–C84	1.367 (9)
N1–C14	1.418 (7)	C32–C33	1.335 (9)	C61–C62	1.384 (7)	C84–C85	1.373 (11)
N1–C9	1.458 (6)	C33–C34	1.432 (7)	C61–C66	1.371 (9)	C85–C86	1.384 (8)
C11–C12	1.416 (7)	C34–C7	1.407 (8)	C62–C63	1.388 (8)	C9–C91	1.488 (6)
C11–C8	1.403 (9)	N4–C41	1.376 (7)	C63–C64	1.372 (11)	C9–C10	1.333 (6)
C12–C13	1.357 (9)	N4–C44	1.377 (6)	C64–C65	1.358 (9)	C91–C92	1.398 (7)
C13–C14	1.413 (7)	C41–C42	1.432 (8)	C65–C66	1.391 (8)	C91–C96	1.381 (8)
C14–C5	1.397 (8)	C41–C7	1.392 (6)	C7–C71	1.492 (8)	C92–C93	1.389 (7)
N2–C21	1.407 (7)	C42–C43	1.346 (7)	C71–C72	1.378 (8)	C93–C94	1.351 (9)
N2–C24	1.396 (5)	C43–C44	1.433 (9)	C71–C76	1.387 (10)	C94–C95	1.391 (8)
N2–C10	1.451 (6)	C44–C8	1.398 (7)	C72–C73	1.368 (10)	C95–C96	1.383 (6)
C21–C22	1.413 (7)	C5–C51	1.485 (8)	C73–C74	1.342 (12)	C10–C101	1.495 (7)
C21–C5	1.396 (6)	C51–C52	1.402 (8)	C74–C75	1.358 (11)	C101–C102	1.385 (9)
C22–C23	1.362 (7)	C51–C56	1.377 (9)	C75–C76	1.388 (11)	C101–C106	1.384 (8)
C23–C24	1.420 (8)	C52–C53	1.388 (9)	C8–C81	1.503 (7)	C102–C103	1.381 (8)
C24–C6	1.392 (7)	C53–C54	1.372 (10)	C81–C82	1.392 (9)	C103–C104	1.374 (10)
N3–C31	1.378 (7)	C54–C55	1.364 (8)	C81–C86	1.391 (7)	C104–C105	1.378 (11)
N3–C34	1.355 (8)	C55–C56	1.384 (9)	C82–C83	1.394 (8)	C105–C106	1.390 (8)
C31–C32	1.439 (7)						

(b) Bond Angles

C11–N1–C14	107.3 (4)	C42–C43–C44	107.9 (5)	C74–C75–C76	119.9 (8)
C11–N1–C9	122.0 (4)	N4–C44–C43	108.8 (4)	C71–C76–C75	119.6 (7)
C14–N1–C9	118.2 (5)	N4–C44–C8	126.1 (5)	C11–C8–C44	128.2 (5)
N1–C11–C12	107.6 (5)	C43–C44–C8	125.0 (4)	C11–C8–C81	115.7 (4)
N1–C11–C8	127.7 (4)	C14–C5–C21	122.4 (5)	C44–C8–C81	116.2 (5)
C12–C11–C8	124.7 (5)	C14–C5–C51	118.4 (4)	C8–C81–C82	121.5 (4)
C11–C12–C13	108.9 (5)	C21–C5–C51	118.6 (5)	C8–C81–C86	119.8 (5)
C12–C13–C14	108.9 (5)	C5–C51–C52	119.5 (5)	C82–C81–C86	118.7 (5)
N1–C14–C13	107.3 (5)	C5–C51–C56	121.2 (5)	C81–C82–C83	121.0 (5)
N1–C14–C5	125.3 (4)	C52–C51–C56	119.3 (5)	C82–C83–C84	119.3 (7)
C13–C14–C5	127.0 (5)	C51–C52–C53	120.2 (6)	C83–C84–C85	120.5 (6)
C21–N2–C24	107.7 (4)	C52–C53–C54	119.3 (6)	C84–C85–C86	120.9 (5)
C21–N2–C10	118.1 (3)	C53–C54–C55	120.7 (6)	C81–C86–C85	119.7 (6)
C24–N2–C10	123.9 (4)	C54–C55–C56	120.8 (6)	N1–C9–C91	113.3 (4)
N2–C21–C22	107.7 (4)	C51–C56–C55	119.7 (5)	N1–C9–C10	119.9 (4)
N2–C21–C22	125.8 (5)	C24–C6–C31	128.2 (4)	C91–C9–C10	125.5 (4)
C22–C21–C5	125.8 (5)	C24–C6–C61	116.7 (5)	C9–C91–C92	116.7 (5)
C21–C22–C23	108.3 (5)	C31–C6–C61	115.0 (4)	C9–C91–C96	123.8 (4)
C22–C23–C24	108.8 (4)	C6–C61–C62	120.9 (6)	C92–C91–C96	119.4 (4)
N2–C24–C23	107.5 (4)	C6–C61–C66	120.4 (4)	C91–C92–C93	120.0 (5)
N2–C24–C6	127.7 (5)	C62–C61–C66	118.6 (5)	C92–C93–C94	120.3 (5)
C23–C24–C6	124.8 (4)	C61–C62–C63	120.6 (6)	C93–C94–C95	120.2 (5)
C31–N3–C34	107.9 (4)	C62–C63–C64	119.9 (5)	C94–C95–C96	120.4 (6)
N3–C31–C32	107.0 (5)	C63–C64–C65	119.9 (6)	C91–C96–C95	119.7 (5)
N3–C31–C6	128.1 (4)	C64–C65–C66	120.4 (7)	N2–C10–C9	120.5 (4)
C32–C31–C6	124.8 (5)	C61–C66–C65	120.6 (5)	N2–C10–C101	113.7 (4)
C31–C32–C33	108.9 (5)	C34–C7–C41	123.8 (5)	C9–C10–C101	124.4 (4)
C32–C33–C34	106.6 (5)	C34–C7–C71	118.3 (4)	C10–C101–C102	117.5 (5)
N3–C34–C33	109.5 (5)	C41–C7–C71	117.8 (5)	C10–C101–C106	122.8 (5)
N3–C34–C7	124.9 (4)	C7–C71–C72	121.3 (6)	C102–C101–C106	119.7 (5)
C33–C34–C7	125.4 (5)	C7–C71–C76	120.7 (5)	C101–C102–C103	119.6 (6)
C41–N4–C44	106.8 (4)	C72–C71–C76	118.0 (6)	C102–C103–C104	120.9 (7)
N4–C41–C42	109.3 (4)	C71–C72–C73	121.6 (7)	C103–C104–C105	119.8 (6)
N4–C41–C7	124.0 (5)	C72–C73–C74	119.4 (7)	C104–C105–C106	119.9 (6)
C42–C41–C7	126.5 (5)	C73–C74–C75	121.3 (7)	C101–C106–C105	120.1 (6)
C41–C42–C43	107.2 (5)				

[a] Numbers in parentheses are esd's in the least significant digits.

and (N2), by 10.6° and 19.9°, respectively. A side-on view of the protonated base indicating the relative orientations of the pyrrole rings is given in Figure 2. It resembles a crab or a flying saucer possessing a C_s pseudosymmetry. This is confirmed by the values of the deviations from the (4N) plane given in Figure 3. The values of the bond lengths in the macrocyclic skeleton are due to its conformation and to the hybridization at the nitrogen atoms. The observed values are consistent with those of equivalent bonds in N-substituted, N,N′-bridged, and protonated porphyrins or metalloporphyrins[6b,7,16,24,27–31] (Table III).

The averaged values of the following bond angles in the porphyrin skeleton also are similar to those found elsewhere: C_α–N–C_α = 107.4 (4), N–C_α–C_β = 108.1 (5), C_α–C_β–C_β = 108.2 (5), N–C_α–C_m = 126.2 (5), C_β–C_α–C_m = 125.5 (5), C_α–C_m–C_p = 117.1 (5)°.[31] The presence of both the bridge and the proton influences the values of the C_α–C_m–C_α angles. For these angles, values between 125 and 127° are normally found.[31] The observed values of 122.4 (5), 128.2 (4), 123.8 (5) and 128.2 (5)° are outside the interval. The opening of two C_α–C_m–C_α angles increases the distances HN3···C10, HN4···C9, HN3···H106, and HN4···H96. The closing of C14–C5–C21 is due to the bridge, whereas the angle

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(29) Hirayama, N.; Takenaka, A.; Sasada, Y.; Watanabe, E.; Ogoshi, H.; Yoshida, Z. *Bull. Chem. Soc. Jpn.* **1981**, *54*, 998–1004.

(30) Hrung, C. P.; Tsutsui, M.; Cullen, D. L.; Meyer, E. F., Jr.; Morimoto, C. N. *J. Am. Chem. Soc.* **1978**, *100*, 6068–6076 and references therein.

(31) Hoard, J. L. In *Porphyrins and Metalloporphyrins*; Smith, K. M., Ed.; Elsevier: Amsterdam, 1975; p 337.

C34–C7–C41 of 123.8 (5)° compares with a normal one. Consequently, the distances between two adjacent nitrogen atoms, N1···N2, N2···N3, N3···N4, and N4···N1, are equal to 2.797 (5), 3.131 (7), 2.776 (6), and 3.114 (6) Å, respectively. The presence of a vinylidene bridge between two pyrrolic nitrogen atoms has only a slight effect on the π-electron delocalization in the porphinato core.

The vinylidene bridge between N1 and N2 completes a new seven-membered ring in the structure. This ring is highly folded along the line passing through N1 and N2 (see Figure 1). Indeed, the dihedral angle between mean plane (B) containing N1, C9, C10, and N2 and mean plane (C) containing N1, C14, C5, C21, and N2 is equal to 53.5°. This folding, in addition to the opening of angles C24–C6–C31 and C44–C8–C11 mentioned above, avoids strong interactions between HN3 and C10 and between HN4 and C9. The observed distances HN3···C10 and HN4···C9 are equal to 2.41 and 2.40 Å, respectively. Steric effects are observed in the bridging group: plane (B), the plane of the bridge, does not contain all the atoms of the olefinic double bond. The atoms C91 and C101 are 0.34 (1) and 0.25 (1) Å out of plane (B). The mean plane (D) containing C9, C10, C91, and C101 forms a dihedral angle of 14.0° with plane (B). Thus interactions H96···N4 (2.75 Å), H106···N3 (2.76 Å), HN3···H106 (2.93 Å), and HN4···H96 (2.82 Å) are reduced. The two phenyl rings attached to the vinylidene bridge are tilted; the values of angles C9–C91–C92, C9–C91–C96, C10–C101–C102, and C10–C101–C106 respectively equal to 116.7 (5), 123.8 (4), 117.5 (5) and 122.8 (5)° best indicate this tilting. All these deformations illustrate the crowding around the bridge, both from the porphyrin nucleus and the lateral phenyl groups. No intermolecular interactions of any chemical significance were found to exist in the lattice.

Experimental Section

General Procedures. Nuclear magnetic resonance spectra were recorded in $CDCl_3$, unless specified, by using Perkin-Elmer R24 and Bruker WP-200 SY (respectively 60- and 200-MHz) spectrometers, and chemical shifts are reported in δ values (ppm from Me_4Si). Coupling constants of pyrrolic and aromatic protons are in the normal ca. 5- or 8-Hz range, respectively, and will not be specified. Visible spectra were taken in CH_2Cl_2 on Hewlett-Packard 8451A and Varian 2200 spectrometers. Elemental analyses were performed by the Service de Microanalyse de l'Institut de Chimie, Strasbourg. Chromatographic separations were performed by using Merck 60 (70–230 or 230–400 mesh) silica gel columns. Most reactions were followed by using Merck F-250 silica gel TLC plates. ***Caution**: Organic perchlorate derivatives may detonate upon scraping or heating.* The preparation of compounds **5**,[14b] **14**,[32] **18**,[14b] **22**,[14b] **26**,[11c] **27**,[11c] **29**,[11c] **30**,[11c] **37**,[11c] and **42**[11c] was described in the literature. Cation radical **9** was purchased from Aldrich. We thank Dr J.-P. Battioni for a generous gift of compound **17**.

Synthesis of 6. Reaction of deoxybenzoin tosylhydrazone and ClCo-TPP according to the literature[11c] gave **6** (74%): ^{1}H NMR δ -1.7 (s, 1 H, vinyl H), 2.92 (t, 2 H), 4.67 (d, 2 H), 5.99 (m, 2 H), 6.25 (m, 3 H), 6.61 (m, 1 H) (side chain 2 C_6H_5), 7.5–8.1 (m, 20 H, meso C_6H_5), 8.81 (s, 8 H, pyrrolic H); visible λ_{max} 414 nm (ϵ 136 000), 530 (13 500). Anal. ($C_{58}H_{39}N_4Co$), C, H, N.

Bridged Porphyrins from 5 and 6. A solution of **5** (75 mg, 0.095 mmol) and **9** (150 mg, 0.184 mmol) in CH_2Cl_2 (60 mL) was stirred at 25 °C for 25 min, concentrated to 10 mL, and poured on top of a silica gel column (50 g in CH_2Cl_2). Elution with CH_2Cl_2–ethyl acetate (95:5) gave **10** (20 mg, 20%; crystallized from CH_2Cl_2–hexane), while CH_2Cl_2–CH_3OH (95:5) eluted **12**. The fraction containing **12** was evaporated, and the residue was dissolved in CH_3OH. Addition of aqueous $NaClO_4$ precipitated a solid which was washed (H_2O), dried under vacuum, and crystallized from CH_2Cl_2–hexane (7 mg, 9%). An identical procedure starting from **6** gave **11** and **13** (respectively 12 and 26%). The relative yields vary considerably, depending on the duration of the separation and by consequence on the transformation of the $SbCl_5$ complex on silica gel.

$SbCl_5$ Complex 10 and Salt 12: ^{1}H NMR δ -2.89 (s, 3 H, CH_3), ca. -2.7 (br signal, 1 H, NH, **12** only), 0.65 (d, 1 H), 4.31 (d, 1 H), 5.46 (t, 1 H), 6.40 (t, 1 H), 6.59 (t, 1 H) (bridge C_6H_5), 7.8–8.5 (m, 20 H, meso C_6H_5), 8.54, 8.74, 8.93, and 8.96 (4d, 4 H, pyrrolic H), 9.05–9.15 (m, 4 H, pyrrolic H); visible λ_{max} 428 nm (ϵ 147 000), 554 (9 500), 592 (14 000), 642 (6 500). Anal. **10** ($C_{53}H_{36}N_4Cl_5Sb$) C, H, N. Anal. **12** ($C_{53}H_{37}N_4ClO_4$ + H_2O) C, H, N.

$SbCl_5$ Complex 11 and Salt 13: ^{1}H NMR (at room temperature) δ ca. -2.5 (br signal, 1 H, NH, **13** only), 2.6 (br signal, 4 H, bridge C_6H_5 *o*-H), 5.94 (br t, 4 H, bridge C_6H_5 *m*-H), 6.36 (t, 2 H, bridge C_6H_5 *p*-H), 7.0–8.4 (m, 20 H, *meso* C_6H_5), 8.78 and 8.83 (AB, 4 H, pyrrolic H), 9.17 and 9.22 (AB, 4 H, pyrrolic H); visible λ_{max} 428 nm (ϵ 160 000), 554 (10 000), 592 (14 700), 640 (6 200). Anal. **11** ($C_{58}H_{38}N_4Cl_5Sb$ + CH_2Cl_2, NMR detected) C, H, N. Anal. **13** ($C_{58}H_{39}N_4ClO_4$ + CH_2Cl_2, NMR detected) C, H, N.

The variable temperature ^{1}H NMR measurements were performed between -50 °C and +50 °C by using salt **13** in $CDCl_3$ solution. The activation barrier was evaluated by using either the ortho or meta signals of the bridge phenyl groups (coalescence at ca. -20 and -30 °C; ΔG^*, calculated by using Eyring formula, 11.5 and 11.1 ± 0.2 kcal mol^{-1}. At -50 °C ortho and meta protons appeared at 1 and 4.1 (ortho) and 5.5 and 6.4 ppm (meta).

The conversion of the $SbCl_5$ complexes **10** and **11** into salts **12** and **13** could be accomplished as follows: (a) addition of silica gel to a solution of **10** (respectively **11**), evaporation of the solvent, heating at ca. 100 °C for a few minutes (the reaction takes 1–3 h at 25 °C), elution with CH_2Cl_2–CH_3OH; (b) addition of *p*-toluenesulfonic acid to a toluene solution or of 1 N HCl to a toluene–CH_3OH solution; (c) heating in refluxing toluene for a few hours. Alternatively salts **12** and **13** are accessible from **5** and **6** by using cation radical **14** (yields similar to the total yields given above).

Cobalt Complex 7. It was prepared in quantitative yeild from corresponding base[11c] which was treated with $Co(OAc)_2$ in boiling CH_2Cl_2–CH_3OH. Evaporation of CH_2Cl_2 followed by precipitation of the product with aqueous NaCl gave **7** which was washed (H_2O), dried under vacuum, crystallized from CH_2Cl_2–hexane, and used as such.

Salt 12 from 7. A solution of **7** (152 mg, 0.185 mmol) and **9** (300 mg, 0.37 mmol) in CH_2Cl_2 (40 mL) was stirred at 25 °C for 20 min. The solution was concentrated to 10 mL and poured on top of a silica gel column (75 g in CH_2Cl_2). The column was kept at room temperature for 3 h to complete the decomplexation of $SbCl_5$. Elution (CH_2Cl_2–CH_3OH, 95:5) gave a reddish green fraction which was purified as described above to give salt **12** (105 mg, 68%).

Preparation of Bridged Octaethylporphyrin 16. A mixture of ClCoOEP (272 mg, 0.43 mmol), deoxybenzoin tosylhydrazone (500 mg, 1.37 mmol), NaOH (600 mg), diglyme (10 mL), and water (1 mL) was stirred and heated at 90 °C for 2 h. After cooling, it was partitioned between toluene and water; the toluene phase was thoroughly washed (H_2O), dried (Na_2SO_4), and evaporated. Crystallization of the residue from CH_2Cl_2–CH_3OH gave **15** (263 mg, 79%; one spot on TLC) used as such. A solution of **15** (120 mg, 0.16 mmol) and **9** (240 mg, 0.3 mmol) in CH_2Cl_2 (50 mL) was kept at room temperature for 3 h. The workup followed the procedure used to isolate **12** and gave **16** (27 mg; 21%): ^{1}H NMR δ ca. -3.5 (br signal, 1 H, NH), 1.54, 1.62, 1.89 and 2.01 (4t, 24 H, CH_3), 2.3 (br s, 4 H, C_6H_5 *o*-H), 3.8–4.6 (m, 16 H, CH_2), 5.69 (t, 4 H, C_6H_5 *m*-H), 6.11 (t, 2 H, C_6H_5 *p*-H), 10.28, 10.51, and 11.22 (3s, 2 + 1 + 1 H, meso H); visible λ_{max} 404 nm (ϵ 80 000), 538 (7 700), 572 (9 600), 616 (4 300). Anal. ($C_{50}H_{55}N_4ClO_4$ + 0.5CH_2Cl_2, NMR detected) C, H, N.

Preparation of ^{13}C-Labeled 11. Benzoic acid, ca. 10% labeled on carboxy group, was prepared[33] from C_6H_5MgBr and $^{13}CO_2$ (from $Ba^{13}CO_3$ and H_2SO_4). Reduction[34] ($LiAlH_4$) and partial reoxidation[35] ($K_2Cr_2O_7$, H_2SO_4, phase transfer) gave $C_6H_5{}^{13}CHO$. Cyanide-catalyzed condensation[36] gave benzoin which was reduced[37] to deoxybenzoin and condensed with tosylhydrazine in CH_3OH. The next steps to **11** are described above. The ^{13}C NMR spectrum (J modulated spin-echo, delay $^1/_2$ J) showed only the quaternary carbons. For unlabeled **11**: ($CDCl_3$) δ 124.40 (bridge), 124.52 (bridge C_6H_5), 126.19, 127.17, and 127.74 (meso), 136.69, 138.75, and 141.18 (meso C_6H_5), 148.52, 148.85, 149.48, and 151.17 (pyrrolic C); (acetone) δ 125.00 (bridge), 125.45 (bridge C_6H_5), 127.10, 127.40, and 128.40 (meso), 137.65, 139.65, and 142.15 (meso C_6H_5), 149.23, 149.63, 150.13, and 151.93 (pyrrolic C). Labeled **11**: only the sharp singles at 124.40 ($CDCl_3$) and 125.00 (acetone) showed the expected signal enhancement.

Vinylcobalt(III) *meso*-Tetraphenylporphyrin (19). We followed the procedure[38] used for the preparation of vinylcobalt(III) octaethyl-

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Table IV. Crystallographic Data

formula	$C_{124}H_{87}Cl_7N_8O_8$	scan type	$\omega/2\theta$
fw	2065.30	scan width, deg	$0.70 + 0.14\mathrm{tg}\theta$
space group	$P\bar{1}$	data collctn range	$2 < \theta < 62°$
a, Å	12.343 (1)	no. of unique data	8066
b, Å	14.172 (2)	no. of data, $I > 3\sigma(I)$	4217
c, Å	16.150 (2)	p	0.08
α, deg	103.96 (1)	no. of refined variables	618
β, deg	110.71 (1)	$R_1 = \sum\|\|F_o\| - \|F_c\|\|/\sum\|F_o\|$	0.067
γ, deg	86.76 (1)	$R_2 = [\sum w(\|F_o\| - \|F_c\|)^2/\sum w\|F_o\|^2]^{1/2}$	0.087
V, Å^3	2563 (2)	esd	1.484
Z	1	largest peak, e Å^{-3} (final difference Fourier map)	0.49
D_{calcd}, g cm^{-3}	1.34		
D_{obsd}, g cm^{-3}	1.33 (1)[a]	largest shift/esd (final least-squares cycle)	0.13
μ (Cu Kα) cm^{-1}	23.1		

[a] Flotation in an aqueous potassium tartrate solution.

porphyrin but started from $[CoTPP]^-$ and acetylene (yield 32%): ^1H NMR δ −1.39, −0.40, and −0.11 (3 dd, 3 H, J = 12, 4.7, and 3 Hz, vinyl), 7.7–8.1 (m, C_6H_5), 8.83 (s, 8 H, pyrrolic H); visible λ_{max} 414 nm (ϵ 124 000), 528 (14 200). Anal. ($C_{46}H_{31}N_4Co$) C, H, N.

Cobalt Complex of *N*-Vinyl-*meso*-tetraphenylporphyrin 20. Vinylcobalt(III) *meso*-tetraphenylporphyrin **19** (100 mg, 0.13 mmol) in CH_2Cl_2 (50 mL) was treated with CF_3COOH (3 mL). After 5 min at room temperature the solution was neutralized (aqueous NH_3), washed (H_2O), dried (Na_2SO_4), and concentrated to a small volume. Chromatography (Merck standardized alumina, 20 g in CH_2Cl_2) gave a green fraction which was evaporated. The base crystallized from CH_2Cl_2–CH_3OH (+5% triethylamine) (47 mg, 51%): ^1H NMR δ −1.64, 1.09, and 1.20 (dd + 2 d, 3 H, J = 15, 8, and 0 Hz, vinyl), 7.74 (s, 2 H, pyrrolic H), 7.8–8.3 (m, 20 H, C_6H_5), 8.45 and 8.61 (AB, 4 H, pyrrolic H), 8.82 (s, 2 H, pyrrolic H). Treatment of this base with $Co(OAc)_2$ (see preparation of **7**) gave **20** (83%). Visible λ_{max} 450 nm (ϵ 128 000), 568 (7 900), 618 (10 700), 666 (6 300). Anal. ($C_{46}H_{31}H_4ClCo$) C, H, N.

Oxidation of 18, 19, and 20. When treated with excess **9** (same conditions as for **5** and **6**) **18**, **19**, or **20** gave several products but none could be identified as a bridged porphyrin.

N-Substituted Complex 22. Porphyrin **21**[14b] (500 mg, 0.59 mmol) was dissolved in CH_2Cl_2 (30 mL) and cooled to −5 °C. After addition of **9** (1 g, 1.2 mmol) the solution was kept at −5 °C for 5 min, concentrated, and chromatographed (silica gel 230–400 mesh; 75 g in CH_2Cl_2). Elution with $CHCl_3$–CH_3OH (98:2) gave a green fraction which was evaporated. The residue was dissolved in CH_3OH. Addition of aqueous NaCl precipitated **22** which was recrystallized from CH_2Cl_2–hexane (142 mg, 27%). Visible λ_{max} 450 nm (ϵ 113 000), 570 (6 000), 630 (9 000), 680 (10 000). Anal. ($C_{54}H_{36}N_4ClCo + H_2O$) C, H, N.

Dihydronaphthylene Bridged Porphyrin 23. To a solution of cobalt complex **22** (46 mg, 0.054 mmol) in CH_2Cl_2 (6 mL) cooled to −5 °C was added **14** (76 mg, 0.124 mmol). The solution was stirred for 3 h during which the temperature raised to +5 °C. Concentration of the solution followed by workup as above for **22** (NaCl replaced by $NaClO_4$) gave **23** (22 mg, 48%): ^1H NMR δ −3.80, −3.22, −1.53, and −0.45 (td, dd, td, dd, 4 H, J = 13 and 5 Hz, CH_2–CH_2), 4.51, 5.28, 6.22, and 6.45 (d, d, t, t, 4 H, aromatic fragment of the bridge), 7.9–8.2 (m, 20 H, meso C_6H_5), 8.68–9.13 (m, 8 H, pyrrolic H); visible λ_{max} 434 nm (ϵ 64 100), 558 (6 600), 594 (8 000), 648 (5900). Anal. ($C_{54}H_{37}N_4ClO_4 + CH_2Cl_2$) H, N, C calcd for 71.30, found 70.55.

Naphthylene Bridged Porphyrin 24. A solution of **23** (20 mg, 0.025 mmol) and dichlorodicyanoquinone (60 mg, 0.26 mmol) in chlorobenzene was refluxed under argon for 24 h. Chromatography over silica gel (50 g, eluent $CHCl_3$–CH_3OH, 97:3) successively gave a little starting material followed by a fraction containing **24** (10 mg, 50%, after usual workup): ^1H NMR δ 2.18, 4.87, 5.50, 6.12, 6.53, and 6.79 (d, d, d, d, t, t, 6 H, naphthylene bridge), 7.6–8.5 (m, 20 H, meso C_6H_5), 8.8–9.2 (m, 8 H, pyrrolic H); visible λ_{max} 436 nm (ϵ 98 700), 562 (7 300), 600 (10 300), 650 (6 500). Although the fit between spectral data and structure was excellent, and although the purity, as appreciated by TLC, seemed to be high, we did not obtain acceptable analytical results for **24**.

Bridged Octaethylporphyrin 25. A mixture of tetralone tosylhydrazone (1.2 g, 3.8 mmol), NaOH (1 g), H_2O (1 mL), and diglyme (10 mL) was stirred and warmed at 90 °C for 1 h. After cooling, it was diluted with H_2O (100 mL) and extracted with pentane (2 × 20 mL). This pentane solution of diazotetraline was washed (2 × 60 mL of H_2O), dried (Na_2SO_4), and added at once to a stirred solution of ClCoOEP (700 mg, 1.2 mmol) in CH_2Cl_2 (70 mL). After 1 min the solvent was evaporated, and the residue dissolved in toluene was filtered through an alumina column (200 g in toluene). This solvent eluted a red product (290 mg, ca. 36%) which was immediately dissolved in CH_2Cl_2 (25 mL), cooled (−5 °C), and oxidized with **9** (780 mg, 0.95 mmol). After 10 min the solution was poured on a silica gel column (200 g in CH_2Cl_2), left for 12 h, and then eluted with CH_2Cl_2–CH_3OH (99:1). Evaporation of CH_2Cl_2 and precipitation from CH_3OH with aqueous $NaClO_4$ gave **25** which was crystallized from CH_2Cl_2–hexane (30 mg, 10%): ^1H NMR δ −4.00, −3.66, −2.02, and −0.69 (td, dd, td, dd, 4 H, J = 16 and 5 Hz, CH_2–CH_2) 1.5–2.0 (m, 24 H, CH_3), 3.95–4.4 (m, 17 H, ethyl CH_2 + 1 Ar H), 5.13, 6.05, and 6.20 (d, t, t, 3 H, Ar H), 10.19, 10.56, 10.77, and 10.98 (4 s, 4 H, meso H); visible λ_{max} 404 nm (ϵ 96 200), 538 (6 800), 572 (9 800), 616 (2 300). Anal. ($C_{46}H_{53}N_4ClO_4$) C, H, N.

When compound **25** and DDQ were heated in refluxing chlorobenzene no more starting material was present after 1 h while simultaneously a solid separated. The absolute insolubility of this material precluded any characterization.

3,4-Dimethoxyphenylcobalt(III) *meso*-Tetraphenylporphyrin (28). 1-Bromo-3,4-dimethoxybenzene (1.8 g, 8.5 mmol) in diethyl ether (20 mL) was treated, at −80 °C and under argon, with *n*-BuLi (8.5 mmol) in hexane (5 mL). The resulting solution was slowly (2 h) warmed to 20 °C and then added to a suspension of ClCoTPP (640 mg, 0.9 mmol) in toluene–diethyl ether 70:30 (80 mL). After 5 min the excess reagent was decomposed by addition of CH_3OH (3 mL), and the solution was concentrated. Addition of CH_3OH gave **28** (634 mg, 87%): ^1H NMR δ −0.45 and −0.14 (d + dd, 2 H, J = 2 and 8 Hz, $(CH_3O)_2C_6H_3$ ortho H), 2.49 and 2.91 (2 s, 6 H, CH_3O), 4.35 (d, 1 H, $(CH_3O)_2C_6H_3$ meta H), 7.6–8.2 (m, 20 H, meso C_6H_5), 8.65 (s, 8 H, pyrrolic H); visible λ_{max} 410 nm (ϵ 142 000), 528 (16 800). Anal. ($C_{52}H_{37}N_4O_2Co$) C, H, N calcd 6.93, found 6.19.

The acid-catalyzed rearrangement[11c] of **28** followed by metalation of the base (see above) gave N-substituted cobalt(II) complex **31** (80%) which was used as such for the cyclization: visible λ_{max} 444 nm (ϵ 84 000), 582 (6 00), 632 (9 300), 688 (5 100).

Attempted Cyclization 27 + 9. To a solution of **27** (77 mg, 0.099 mmol) in CH_2Cl_2 (100 mL) was added **9** (150 mg, 0.184 mmol). The solution turned immediately green (formation of mono-N-substituted porphyrin) and was kept at 20 °C for a week during which a green product of low polarity formed at the expense of the polar one. Concentration of the solution and chromatography (silica gel, 40 g in CH_2Cl_2) gave **32** (eluted with CH_2Cl_2–AcOEt, 95:5) which was crystallized from CH_2Cl_2–hexane (56 mg, 55%): ^1H NMR δ −2.9 (br s, 1 H, NH), 2.15 (d, 2 H, N-aryl ortho H), 2.70 (s, 3 H, OCH_3), 4.48 (d, 2 H, N-aryl meta H), 7.7–8.5 (m, 20 H, meso C_6H_5), 8.22 (s, 2 H, pyrrolic H), 8.74 (s, 2 H, pyrrolic H), 8.83 and 8.85 (AB, 4 H, pyrrolic H); visible λ_{max} 443 nm (ϵ 181 000), 602 (9 100), 664 (18 000). Anal. ($C_{51}H_{36}N_4Cl_5OSb$) C, H, N.

Compound **38** was obtained independently from *N*-anisyl-*meso*-tetraphenylporphyrin[11c] (20 mg, 0.028 mmol) and excess $SbCl_5$ (0.5 mL) in CH_2Cl_2 (10 mL). Filtration of the solution over silica gel (10 g, eluent CH_2Cl_2–AcOEt, 95:5) gave **32** (16 mg, 56%) found to be identical with the product from **27** (TLC, ^1H NMR, visible).

Bridged Porphyrin 33. A solution of **29** (643 mg, 0.76 mmol) and **14** (1.5 g, 2.4 mmol) in 1,1,2,2-tetrachloroethane (55 mL) was heated under reflux for 70 h. After having been cooled to 60 °C, $Co(OAc)_2$ (10 equiv/porphyrin, in a minimal amount of warm CH_3OH) was added to metalate the free base **40** formed during the reaction (this complexation takes less than 5 min). The crude mixture was cooled to 25 °C and absorbed on silica gel (ca. 300 g in CH_2Cl_2). Elution with CH_2Cl_2–CH_3OH (98:2) gave the starting material (14%; including the metalated base) which was precipitated from CH_3OH with aqueous NaCl (or

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aqueous $NaClO_4$ to produce the corresponding perchlorate). CH_2Cl_2–CH_3OH (95:5) eluted the bridged porphyrin **33** which was precipitated from CH_3OH with aqueous $NaClO_4$, washed (H_2O), and crystallized from CH_2Cl_2–hexane (394 mg, 66%): ^1H NMR δ ca. −3.7 (br signal, 1 H, NH), 2.37 and 4.51 (AA'XX', 2 H + 2 H, phenylene), 7.8–8.3 (m, 20 H, meso C_6H_5), 8.85 and 8.93 (AB, 4 H, pyrrolic H), 9.01 and 9.09 (AB, 4 H, pyrrolic H); visible λ_{max} 442 nm (ϵ 93 000), 566 (7 800), 602 (12 000), 656 (6 300). Anal. ($C_{50}H_{33}N_4ClO_4 + H_2O$) C, H, N.

The same procedure, when applied to the corresponding starting material in the OEP series, did not yield any bridged porphyrin.

Bridged Porphyrin 34. A solution of **31** (50 mg, 0.055 mmol) and **14** (100 mg, 0.16 mmol) in 1,2-dichloroethane (12 mL, filtered through a bed of alumina) was heated under reflux for 36 h. Workup as for **33** gave **34** (18 mg, 38%): ^1H NMR δ ca. −3.6 (br signal, 1 H, NH), 1.81 (s, 2 H, phenylene), 2.25 (s, 6 H, OCH_3), 7.8–8.25 (m, 20 H, meso C_6H_5), 8.85 and 8.93 (AB, 4 H, pyrrolic H), 8.96 and 9.05 (AB, 4 H, pyrrolic H); visible λ_{max} 436 nm (ϵ 114 000), 562 (8 300), 600 (11 700), 650 (7 300). Anal. ($C_{52}H_{37}N_4ClO_4 + CH_2Cl_2$) C, H, N.

Preparation of Metallo-*N*-phenyl-*meso*-tetraphenylporphyrin's 36, 39, and 40. Copper complex **36** was obtained (as above from cobalt) from **41** and $Cu(OAc)_2$ [visible λ_{max} 456 nm (ϵ 115 600), 554 (10 100), 600 (9 400), 670 (4 100). Anal. ($C_{50}H_{33}N_4ClO_4Cu$) C, H, N]. Metalation of **41** with $FeCl_2$ according to Lavallee et al.[22b] gave **38** whose spectral data are identical with those described in the literature.[10e] The nickel complex **39** was isolated as its perchlorate following the usual procedure [visible λ_{max} 448 nm (ϵ 81 100), 562 (7 500), 625 (7 000), 688 (4 400). Anal. ($C_{50}H_{33}N_4ClNi$) C, H, N]. The manganese complex **40** was prepared by using Adler's procedure[39] ($Mn(OAc)_2$ in refluxing DMF) [visible: λ_{max} 452 nm (ϵ 120 000), 580 (6 700), 642 (11 400), 690 (8 400). Anal. ($C_{50}H_{33}N_4ClMn$) C, H, N]. The cyclization conditions described above for the preparation of **33** were applied to **36–41**. Only **40** gave 10% **33**.

One-Step Preparation of 33. A solution of ClCoTPP (100 mg, 0.14 mmol) and ABT[9a] (200 mg, 1.5 mmol) in 1,1,2,2-tetrachloroethane (4 mL, filtered through a bed of alumina) was heated under dry air at 100 °C for 3 days. Workup as above gave **33** (35 mg, 29%) and **29** (18 mg, 16%). When the same reaction was run in the presence of tetraphenylcyclopentadienone (3 mmol), no spot (TLC) corresponding to TPN could be detected (We checked that when ca. 10 μL of a 2×10^{-6} M solution of TPN was deposited on TLC, a faint spot was still visible under UV light; this corresponds to ca. 2×10^{-4} mg). Two major colorless compounds whose polarity was between those of the ketone and the porphyrinic products could be crystallized. They were not fully characterized, but MS and NMR spectra indicated a composition corresponding to ketone + ABT − H_2. The same products formed when the reaction was run in the absence of ClCoTPP.

Electrochemical Measurements. To obtain half-wave potentials we used a Bruker E 130 apparatus equipped with three electrodes: Pt rotating electrode (Tacussel, area 3.4 mm², 0–5000 rev·min⁻¹), a Pt wire as counter electrode, and a calomel reference electrode (in saturated aqueous KCl) connected to the electrochemical cell by a bridge containing the solvent and the supporting electrolyte. The coulometric experiments were run by using a SOLEA 100 1X potentiostat. The electrode was a Pt grid, and the counter electrode was isolated from the solution by a fritted glass. The solvents were of the highest commercially available quality, and the supporting electrolyte, $n\text{-}Pr_4N^+ClO_4^-$ (0.1 M), was recrystallized from ethanol and dried for 2 days at 80 °C under vacuum. All operations were run under a dry argon atmosphere. At the end of the electrolyses the solutions were washed (H_2O, 6 times by using 3 × the volume of the organic phase), dried (Na_2SO_4), and submitted to the normal isolation procedure. The ESR measurements were performed at −196 °C in 1,2-dichloroethane + 0.1 M $n\text{-}Pr_4N^+ClO_4^-$ (electrolysis medium) by using a Bruker ER 420 spectrometer. The signal observed for **29** showed $g = 2.0035$, width 68.5 G.

Phenylene-Bridged OEP 43. *N*-PhOEP[11c] (35 mg, 0.05 mmol) was quantitatively metalated with $Co(OAc)_2$, and the complex was isolated as its perchlorate which was immediately electrolyzed in 1,1,2,2-tetrachloroethane (50 mL + 0.5 g $n\text{-}Pr_4N^+ClO_4^-$) at 120 °C for 44 h. The solution was heated at 120 °C for a further 30 h. After cooling, the usual isolation procedure was followed to yield **43** (1 mg, 3%): ^1H NMR δ ca. −4.5 (br signal, 1 H, NH), 1.72, 1.85, 1.88, and 1.98 (4 t, 24 H, CH_3), 1.96 and 4.25 (AA'XX', 4 H, bridge C_6H_4), 3.9–4.55 (m, 16 H, CH_2), 10.06, 10.85, and 10.89 (3 s, 2 + 1 + 1 H, meso); visible λ_{max} 410 nm (ϵ 77 600), 542 (6 700), 576 (8 700), 624 (2 500); MS (chemical ionization, NH_3), m/e = 609 (M − ClO_4).

Collection and Reduction of X-ray Data for 13. Crystals suitable for X-ray diffraction studies were obtained from slow diffusion of hexane into a CH_2Cl_2–chlorobenzene solution at room temperature. A crystal with dimensions 0.14 × 0.16 × 0.22 mm was sealed in a Lindemann glass capillary and mounted on an Enraf-Nonius CAD4 diffractometer. A summary of crystal and intensity data is presented in Table IV. The automatic locating and centering of 25 reflections ($17 < \theta < 29°$) followed by least-squares analyses of the setting angles produced accurate unit cell parameters, indicating triclinic crystal system. The $P\bar{1}$ space group was confirmed by the subsequent refinement of the structure.

A unique set of diffraction data was collected (Cu Kα radiation, graphite monochromator). The intensities of three standard reflections were measured every 2 h of X-ray exposure time, and no decay was observed. The intensity data were processed as described in *CAD4 and SDP-PLUS User's Manual*.[40] The net intensities and their standard deviations were corrected for Lorentz-polarization effects. An empirical absorption correction was applied by use of ψ scans for χ values near 90°. The maximum, minimum, and average transmission factors obtained are 1.00, 0.92, and 0.97, respectively.

Solution and Refinement of the Structure. The structure was solved by direct methods. A total of 56 out of 73 non-hydrogen atoms were found on the best E map. From a three-dimensional electron density map, the positions of 14 more atoms were obtained. Subsequent structure factor calculations and Fourier syntheses revealed the position of the remaining non-hydrogen atoms. The atomic scattering factors were taken from the usual tabulation,[41a] and the effects of anomalous dispersion were included by using Cromer and Ibers'[41b] values of $\Delta f'$ and $\Delta f''$.

The chlorobenzene molecule resides on a position of $\bar{1}$ symmetry, and its chlorine atom ClS was treated as two half atoms. Some difficulties were encountered with the dichloromethane molecule, in which one chlorine atom appeared disordered. Refinement was conducted with a model in which this chlorine was refined as three third atoms: Cl2, Cl3, Cl4. The observed values for the angles Cl1–C–Cl*n* (*n* = 2, 3, 4) are near 109° (112.4 (6), 105.0 (6), 113.2 (7)°). The non-hydrogen atoms of the dichloromethane molecule were refined isotropically, while all other non-hydrogen atoms including those of the chlorobenzene molecule were refined anisotropically. The function minimized was $\sum w(|F_o| - |F_c|)^2$, where $|F_o|$ and $|F_c|$ are the observed and calculated structure amplitudes and $w = 1/[\sigma(F_o)]^2$. After successive full-matrix least-squares refinement cycles, the positions of the hydrogen atoms, except those of the hydrogens on the dichloromethane molecule and of the proton on the porphyrin nitrogen atom, were calculated and verified on a difference Fourier synthesis. They were introduced with fixed idealized geometry (C–H = 0.95 Å and B = 5 Å²) but not refined. Further cycles of refinement yielded $R_1 = 0.074$ and $R_2 = 0.096$. At this stage, a difference Fourier synthesis map revealed two peaks, located 0.9 Å from N3 and N4, respectively. Both were introduced as hydrogen with B = 5 Å² and an occupancy of a half and not refined. The final refinement converged to values of R1 and R2 of 0.067 and 0.087, respectively. The final values of the positional parameters, anisotropic thermal parameters for non-hydrogen atoms, and a listing of the observed and calculated structure amplitudes are available as Supplementary Material.[42]

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Supplementary Material Available: Listings of positional parameters, anisotropic displacement parameters for non-hydrogen atoms, and a table with least-squares mean planes for $(C_{58}H_{39}N_4)(ClO_4)\cdot(CH_2Cl_2)\cdot{}^1/_2(C_6H_5Cl)$ (6 pages); listing of observed and calculated structure factors (22 pages). Ordering information is given on any current masthead page.

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(40) All crystallographic work was done at the Laboratoire de Cristallographie Biologique, I.B.M.C. du C.N.R.S. Instrumentation consists of an Enraf-Nonius CAD4 diffractometer controlled by a DEC PDP 8/A with a RL01 disk. The Enraf-Nonius software used is described in *CAD4 Operation Manual*; Enraf-Nonius: Delft, Amsterdam, 1977 (updated in Jan 1980). All calculations were carried out on a DEC PDP 11/44 equipped with three disk drives (a RM02 and two RL02 disk drives), a Versatec printer/plotter, and a Plessey Kennedy 9000 tape drive with the use of the Enraf-Nonius CAD4-SDP-PLUS programs. This crystallographic computing package is described by: Frenz, B. A. In *Computing in Crystallography*; Schenk, H., Olthof-Hazekamp, R. O., van Konigsveld, H., Bassi, G. C., Eds.; Delft University Press: Delft, Holland, 1978; pp 64–71. Frenz, B. A. In *Structure Determination Package and SDP-PLUS User's Guide*; Frenz, B. A. & Assoc., Inc.: College Station, TX, 1982.

(41) (a) Cromer, D. T.; Waber, J. T. *International Tables for X-ray Crystallography*; Kynoch: Birmingham, England, 1974; Vol. IV, Table 2.2B. (b) Cromer, D. T.; Ibers, J. A. *International Tables for X-ray Crystallography*; Kynoch: Birmingham, England, 1974; Vol. IV, Table 2.3.1.

(42) Supplementary material, see paragraph at the end of this paper.