structure factor calculations at their calculated positions. The positional and anisotropic thermal parameters were refined by block-matrix/full-matrix procedures.

The atomic scattering factors were those from ref 35 modified for the real and imaginary parts of anomalous dispersion.

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Acknowledgment. This material is based upon work supported by the National Science Foundation under Grant CHE-8401844 (R.J.A.). X-ray diffraction studies were supported by the U.S. Department of Energy, Office of Basic Energy Sciences, Materials Sciences Division, Under Contract W-7405-ENG-82. We thank Dr. N. Kostić for helpful discussions.

Supplementary Material Available: Tables of positional parameters, anisotropic thermal parameters, all bond distances and angles, and structure factors (32 pages). Ordering information is given on any current masthead page.

Coreceptor Molecules. Synthesis of Metalloreceptors Containing Porphyrin Subunits and Formation of Mixed Substrate Supermolecules by Binding of Organic Substrates and of Metal Ions

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Abstract: Three coreceptor molecules, two macrotetracycles **1** and **2** and one macropentacycle **3**, containing [18]-N_2O_4 macrocyclic and porphyrinic subunits, have been synthesized and characterized. They form metalloreceptors by complexation of transition-metal ions like Zn(II) or Cu(II) with the porphyrin groups. Binding of α,ω-diammonium cations to the [18]-N_2O_4 units occurs with substrate inclusion, yielding η^2-cryptates like **27**, **28**, and **31**, as indicated by very large upfield shifts of the CH_2 proton NMR signals of the substrates. Similarly, these organic cations also bind to the Zn(II)-containing metalloreceptors **19**, **20**, and **22**, giving organic/inorganic *mixed substrate supermolecules*, such as **29**, **30**, and **32**. In these and similar species, the simultaneous complexation of several substrates opens the way to the study of mutual interactions within supramolecular structures and of regulation effects on physical and chemical properties.

Beyond receptor molecules possessing a single binding unit, the chemistry of molecular receptors enters the domain of polytopic coreceptors, macropolycyclic molecules incorporating several binding subunits which may cooperate for the complexation of either several singly bound substrates or of multiply bound polyfunctional substrates.[1,2] Homotopic coreceptors which bind terminal diammonium cations and dicarboxylate anions by means of two identical subunits have been described (see references in ref 1 and below).

Metalloreceptors are heterotopic coreceptors which combine suitable substrate selective binding subunits, such that they can complex both organic substrate(s) and metal cation(s), thus forming mixed substrate supermolecules. As a consequence, interactions and reactions may take place between metal-centered reactive sites and co-bound molecular substrate(s). Such metalloreceptors, -reagents, and -catalysts may also mimic features of metalloproteins.

Earlier examples of a process which may be considered to be of the metalloreceptor type were the formation of molecular cation-anion pairs by a cascade mechanism which involved first complexation of one or two metal cations to a neutral aporeceptor followed by ion pairing between the resulting holoreceptor cation and a molecular anion.[3,4]

We have designed and studied in recent years several metalloreceptor systems (for brief descriptions see ref 1 and 2). We now describe the synthesis of the three coreceptors **1-3** and report their ability to complex *both* metal cations and primary diammonium ions, by means of porphyrin and macrocyclic [18]-N_2O_4 (**12**) subunits, respectively.[5,6]

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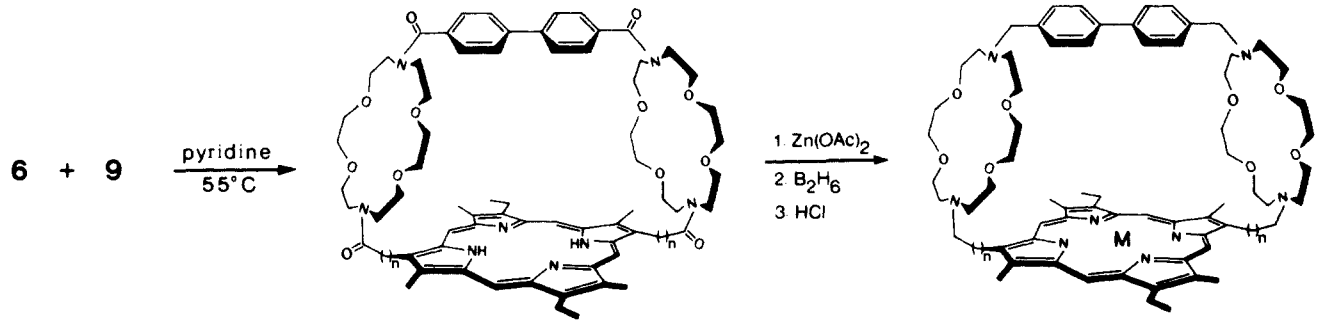
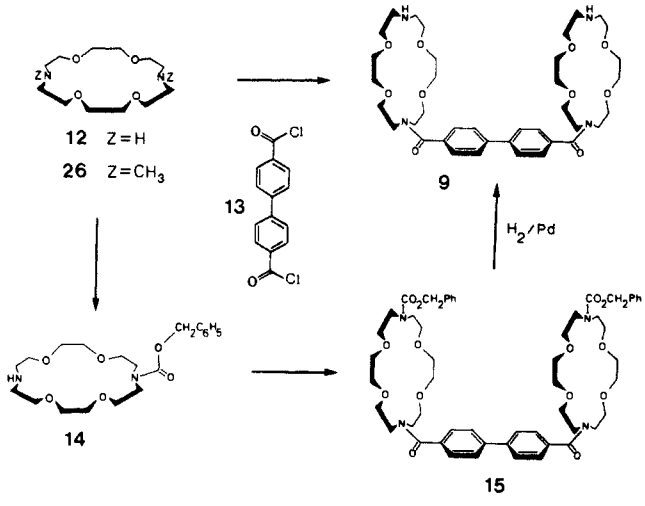
Scheme I



10 n=1
11 n=2

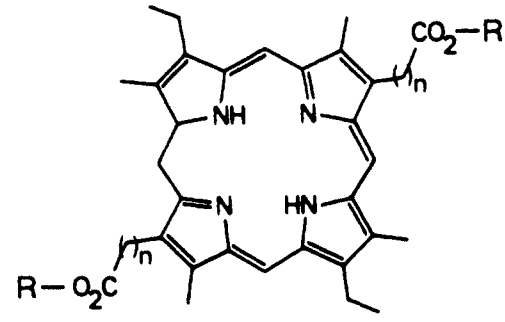
1 n=1, M=2H
2 n=2, M=2H
19 n=1, M=Zn
20 n=2, M=Zn
21 n=1, M=Cu

Scheme II



Results

Synthesis of Metalloreceptors 1–3. The synthetic route used to obtain the macrotetracycles **1** and **2** is shown in Scheme I. It follows the strategy that allows introduction of different bridges between the two macrocyclic subunits of a cylindrical macrotricycle (see Figure 7, route A, in ref 7). The porphyrin dicarboxylic acids **4** and **5** were prepared according to the literature[8,9] and subsequently activated by conversion to the bis(*p*-nitrophenyl) esters **6** and **7**[10] which by condensation with the biphenylene-bridged bis-[18]-N_2O_4 macrocycle **9** in warm pyridine[10,11] under conditions of moderate dilution led to the tetraamides **10** and **11**, respectively. Good yields were obtained for these condensations provided long reaction times were employed (up to 48 h were required to reach completion); because of the slow nature of the coupling reaction, the reactants were simply mixed together at the outset of the reaction. The tetraamides **10** and **11** could be obtained in pure form following careful chromatography on silica gel and recrystallization from a dichloromethane–hexane mixture. In general, however, the crude products could be used directly for further synthetic work.



4: *n* = 1; R = H
5: *n* = 2; R = H
6: *n* = 1; R = *p*-$C_6H_4NO_2$
7: *n* = 2; R = *p*-$C_6H_4NO_2$
8: *n* = 1; R = CH_2CH_3

The tetraamines **1** and **2** were obtained from the tetraamides **10** and **11** by using a three-step sequence which involved (i) preparation of the zinc(II) derivatives, (ii) reduction with diborane, and (iii) treatment with concentrated HCl to effect hydrolysis and demetalation. The reduction of the amides proceeded smoothly if this three-step sequence was employed; the crude yields were nearly quantitative. Only poor yields were obtained, however, if the free-base porphyrins were treated directly with diborane. Formation of the zinc complex serves to protect the porphyrin macrocycle from reaction with diborane. Compounds **1** and **2** were obtained in analytically pure, crystalline form following chromatography on alumina and slow recrystallization from a dichloromethane–hexane mixture. A minimum of alumina was used as poor recoveries were observed on this support. Overall, yields of 54% and 45% were obtained for **1** and **2** (based on **6** and **7**).

The bis-macrocycle compound **9** was prepared by two methods (Scheme II). The first utilized a direct reaction between dichloroformyl-4,4′-biphenyl (**13**) and the [18]-N_2O_4 macrocycle **12**. The second involved treatment of the monoprotected [18]-

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Scheme III

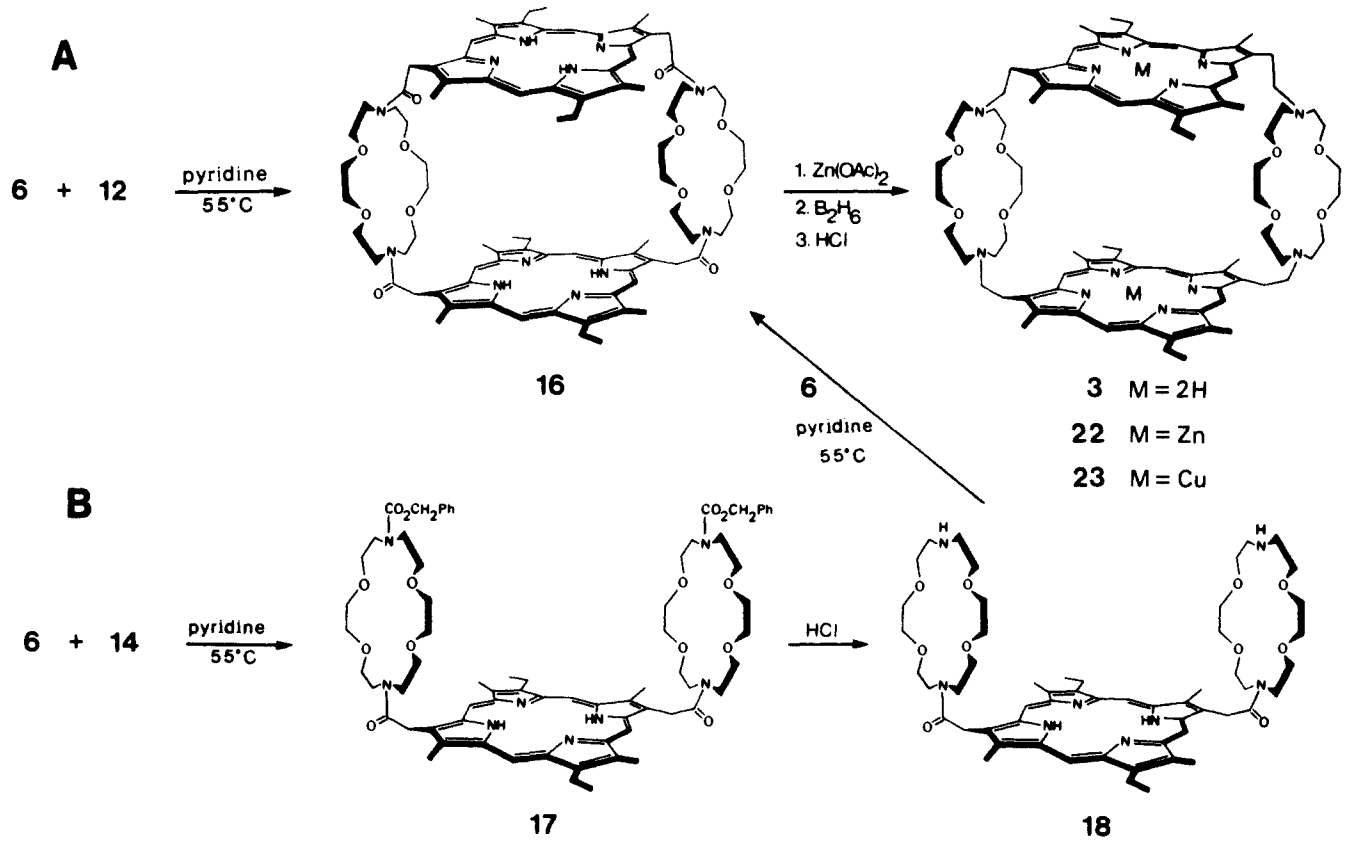

Table I. Electronic Spectral Data for Porphyrin-Containing Heterotopic Coreceptors in Chloroform [λ_{max} in nm (log ϵ)] and a Reference Compound

metal	receptor	soret	visible			
2H	**1**	375 (sh), 397 (5.15)	497 (4.04)	532 (3.90)	567 (3.69)	619 (3.53)
	2	374 (sh), 397 (5.21)	497 (4.12)	531 (3.98)	567 (3.72)	619 (3.61)
	3	388 (4.86)	502 (4.21)	536 (4.03)	571 (3.90)	623 (3.71)
	8[a]	400	498	536	566	620
Zn	**19**	405 (5.41)		536 (4.17)	572 (4.17)	
	20	402 (5.39)		536 (4.17)	572 (4.22)	
	22	385 (5.39)		537 (4.07)	572 (4.32)	
Cu	**21**	399		525	563	
	23	390		530	556	

[a] From ref 15.

N_2O_4 macrocycle **14**[12] with **13** to give **15**, which, after hydrogenolysis, afforded **9**. Although both routes proceeded in good yield, we favor the latter stepwise approach in that the product **9** was obtained in higher purity.

Two strategies were employed to synthesize the macropentacyclic tetraamine **3**. Both involved the generation and subsequent reduction of the tetraamide **16**, as outlined in Scheme III. In method A, the key tetraamide **16** (along with numerous impurities) is produced directly by condensing the activated porphyrin **6**[10] with the [18]-N_2O_4 macrocycle **12** under conditions of high dilution. When this reaction was carried out on small scale, the intermediate **16** could be purified by careful chromatography on silica gel. On larger scales, however, the low solubility of **16** in common organic solvents precluded such purifications. In practice, therefore, the crude reaction mixture was subjected directly to the three-step reducing procedure outlined above. Complete purification was then effected at the terminal tetraamine stage. The tetraamine **3** is far more soluble than the tetraamide precursor **16** and could be purified by repeated chromatography on alumina (using a minimum of support to avoid substantial material losses) followed by a recrystallization from dichloromethane/hexane. Unfortunately, the yields of **3** obtained by this direct condensation approach (method A, Scheme III) were low (ca. 10% based on **6**).

Satisfactory yields of **3** were obtained by using a stepwise procedure (method B, Scheme III). In this approach, the monoprotected [18]-N_2O_4 compound **14**[12] is first condensed with the activated porphyrin **6**[10] to yield the porphyrin-bridged, bismacrocyclic compound **17** in good yield. Standard methods (e.g., H_2/Pd or HBr/HOAc) failed to cleave the carbobenzoxy protecting group cleanly. Deprotection could be effected smoothly by treatment with a mixture of concentrated hydrochloric and trifluoroacetic acids. The reaction was monitored carefully as under these conditions the rate of amide hydrolysis is apparently close to that of carbamate cleavage. In favorable cases, the crude diamide–diamine **18** was obtained in sufficient purity for use in the subsequent steps. When required, purification was effected by chromatography on alumina. A second condensation reaction with **6**[10] then gave the intermediate tetraamide **16**, in a relatively pure state. After reduction, the final purifications of **3** were far easier than those required when the direct condensation approach was employed. The overall yield of **3** with use of the stepwise procedure was ca. 25% (based on the monoprotected macrocycle **14**).

Formation of the Metalloporphyrin Complexes. In general, as metal binding to a porphyrin site occurs, the four absorptions in

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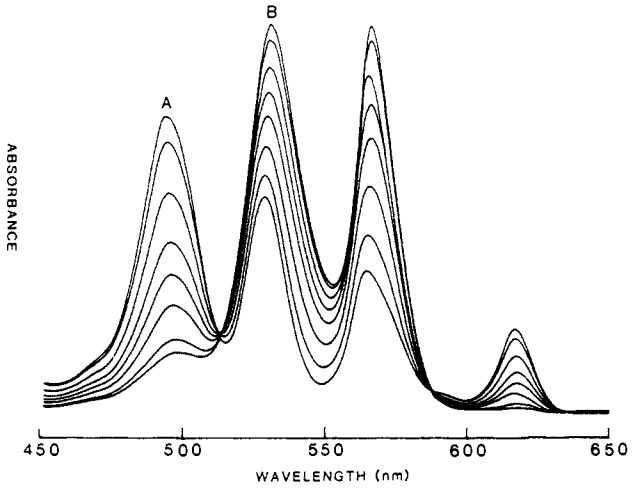

Figure 1. Spectrophotometric titration of **1** with zinc acetate: generation of *metalloreceptor* **19**. Curve A; **1**. Curve B; **19**, obtained by the addition of 1.05 equiv of zinc(II). Intermediate curves obtained by adding increasing quantities of zinc acetate in CH_3OH to the initial solution of **1** in $CHCl_3$. Spectra were recorded with use of a gas-tight cuvette maintained at 40 °C for 30 min between runs.

the 450–700-nm region disappear and are replaced by one or, more frequently, two bands.[13] Electronic spectroscopy was therefore used to demonstrate the formation of the zinc(II) and copper(II) derivatives **19–23** of the free-base porphyrins **1–3**. Spectral data for these complexes are given in Table I.

The zinc(II) porphyrin complexes were produced cleanly. For instance, when a solution of the tetraamine **1** in chloroform, maintained at 40 °C in a gas-tight cuvette, was titrated over the course of several hours with 1 equiv of zinc(II) acetate in methanol, complete conversion to the zinc(II) derivative **19** was achieved (Figure 1). That clean isosbestic behavior was observed during the course of the titration suggests that metal insertion into the porphyrin unit occurred quantitatively without competing complexation into the [18]-N_2O_4 macrocyclic sites. Similar isosbestic behavior was observed when either **2** or **3** was titrated under similar conditions with 1 equiv of zinc(II) acetate per porphyrin group.

When analogous titrations of **1** and **3** were performed with copper(II) acetate, isosbestic behavior was not observed. Apparently copper binding into the [18]-N_2O_4 sites competes with incorporation into the porphyrin unit. This finding is consistent with the observation that the [18]-N_2O_4 macrocycle, **12**, displays an ca. 10^4 higher affinity for Cu(II) than for Zn(II).[14] The copper(II) cation bound in the [18]-N_2O_4 sites is more labile than that held in the porphyrin macrocycle. It thus proved possible to prepare the pure copper porphyrin complexes, **21** and **23**, by adding an excess of copper(II) acetate dissolved in MeOH to solutions of the porphyrins **1** and **3** in boiling $CHCl_3$ and then washing the solutions with aqueous sodium cyanide.

Characterization of the Receptors 1–3 and of Their Metal Complexes 19–23. UV-Visible Absorption Spectra. UV–visible spectral data for the three porphyrin-containing receptors and for their metal complexes described in this report are summarized in Table I. The electronic spectra of the free-base compounds **1** and **2** display etio-type features which are typical of monomeric porphyrins with 6 or more alkyl groups in the β-pyrrolic positions.[13] Specifically, an intense Soret at λ_{max} 397 nm and four satellite bands of decreasing intensity in the region between 500 and 700 nm were observed. An essentially etio-type spectrum was also displayed by the dimeric porphyrin compound **3**. In this case,

Table II. Representative ^1H NMR Data for Porphyrin-Containing Receptors and Reference Compounds

	chemical shift,[a] ppm			
compd	NH (pyrrole)	CH_3 (ring)	H (meso)	H (phenyl)
8[b]	−3.75	3.67	10.10, 10.16	
24[c]				7.35, 7.40
1	−3.74	3.54	10.02, 10.09	5.90, 6.41
2	−3.69	3.62, 3.64	10.06, 10.13	6.41, 6.66
3	−4.39	2.85, 3.04	8.30, 9.76	

[a] In $CDCl_3$ at 200 MHz, unless otherwise noted. [b] In $CDCl_3$ at 100 MHz, from ref 10. [c] In $CDCl_3$ at 250 MHz, from ref 17.

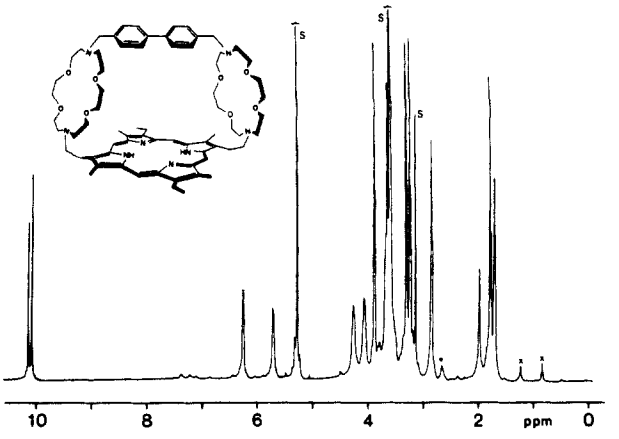

Figure 2. Proton NMR spectrum of receptor **1** at 400 MHz (CD_2Cl_2:CD_3OD 9:1 (v/v)). Due to exchange, no signals for the internal pyrrole N–H protons are observed in this solvent system. Peaks marked with x and S are due to impurities and solvent, respectively. For assignments of the other peaks, see Experimental Section.

however, the Soret band was broadened and blue shifted by 11 nm and the visible bands slightly red-shifted as compared to the monomers **1** and **2**, or to the diethyl ester **8**.[15] Such spectral shifts have previously been observed for "face-to-face" dimeric porphyrin systems in which the two prophyrin subunits are covalently constrained to adopt a close orientation.[10,15,16] Both the zinc(II) and copper(II) derivatives of the dimeric porphyrin receptor (**22** and **23**) also had blue-shifted Soret bands as compared to the corresponding monoporphyrin complexes (i.e., **19**, **20**, and **21**).

^1H NMR Spectra. ^1H NMR spectroscopy was used to characterize the porphyrin-containing receptors **1**, **2**, and **3**. With exception of the tetraamides **10**, **11**, and **16** which displayed poorly resolved spectra, all intermediates reported in this study were also characterized by ^1H NMR spectroscopy. Peak assignments were made on the basis of integrations, spectral intercomparisons of similar compounds, and homodecoupling studies. Selected data are summarized in Table II; complete tabulations for each compound are included in the Experimental Section.

In the spectra of **1** and **2** signals due to both the biphenyl and porphyrin subunits are clearly discernable (Figure 2). Of particular interest are the peaks ascribable to the two nonequivalent biphenyl protons. As compared to the analogous bis-biphenyl

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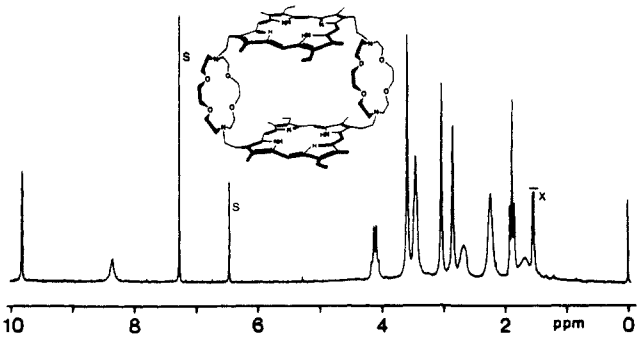
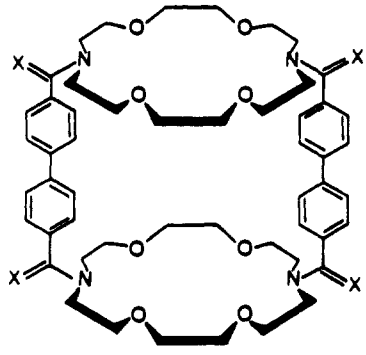


Figure 3. Proton NMR spectrum of receptor **3** at 200 MHz ($CDCl_3$); the signal of the internal NH protons is observed upfield at −4.39 ppm.

receptor **24**,[17] these signals are shifted upfield by 0.94 and 0.74 ppm for **2** and 1.45 and 0.99 ppm for **1**. These upfield shifts suggest that the biphenyl protons of **1** and **2** are shielded by the porphyrin macrocycle and imply that in solution, as in the crystalline state (vide infra), the biphenyl subunits lie above the porphyrin rings.



24: X = 2H
25: X = O

Shielding effects are also observed in the case of the dimeric porphyrin receptor **3** (Figure 3). For instance, the internal pyrrole protons resonate at 0.55 ppm higher field in the dimer **3** than in the monomer **1**, a behavior which is qualitatively consistent with that observed for several covalently linked, cofacial porphyrin dimers.[10,16] This suggests that conformations which allow for complete or partial overlap of the two porphyrin macrocycles occur in solution. In the dimer **3** several other signals, including those of the meso and porphyrin methyl protons, are also shifted to higher field (Table II).

As is the case for the members of the β-linked "face-to-face" dimeric porphyrin series,[9,10,16c,d,e,h] compound **3** could exist as a mixture of two diastereomers in which the relative orientation of the two rings is different. Space filling molecular models suggest, however, that ring flipping and interconversion between the two forms is possible in the case of **3**. For a mixture of two diastereomeric β-linked porphyrins, up to eight signals are possible for the meso protons. Although somewhat broadened as compared to the monomers **1** and **2**, only two peaks are observed in this region for the dimer **3**. At present it is difficult to ascertain if only one diastereomer is produced in the coupling reaction, or if, more likely, the two diastereomers which might be formed interconvert rapidly on the NMR time scale.[18]

The zinc(II) derivatives **19**, **20**, and **22** are diamagnetic and their ^1H NMR spectra were recorded. In general, the basic spectral features were similar to those of the free-base compounds **1–3**. Although no efforts were made to make detailed assignments,

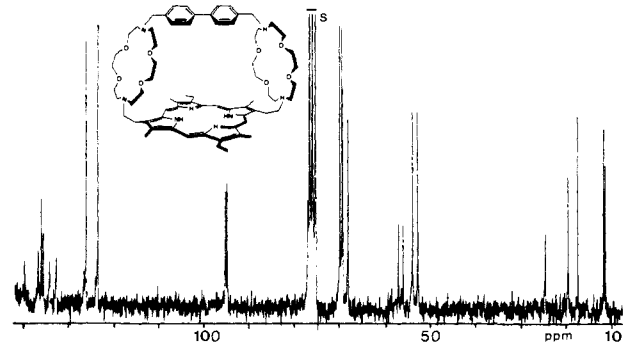


Figure 4. ^{13}C NMR spectrum of **1** at 50 MHz ($CDCl_3$). Peaks marked with S are due to solvent. For peak assignments, see Experimental Section.

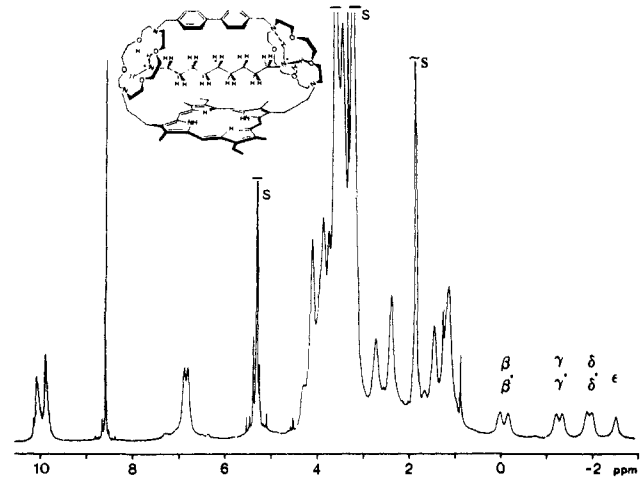


Figure 5. ^1H NMR spectrum at 200 MHz (CD_2Cl_2:CD_3OD 9:1 (v/v)) of the supramolecular complex **27** formed from the receptor **1** and the S_9^{2+} substrate ^+H_3N-$(CH_2)_9$-NH_3^+ dipicrate.

it is to be noted that the spectra of these complexes displayed no signals corresponding to the internal pyrrole protons and hence no peaks upfield of Me_4Si.

^{13}C NMR Spectra. Well-resolved ^{13}C NMR spectra, which are consistent with the proposed structures, were obtained for the receptors **1–3** and several key intermediates. For instance, the ^{13}C NMR of **1** is shown in Figure 4. Tentative peak assignments for these compounds were made on the basis of intercomparisons and by analogy to simpler compounds; these data are included in the Experimental Section. In general, the ^{13}C signals of the receptors **1** and **2** lie within 3 ppm of those for appropriate reference compounds (e.g., **8** and **26**). Exceptions are the two signals of carbons 1 and 4 of the biphenyl moiety. Compared to the bis-biphenyl receptor, **24**,[17b,19] these signals are split and shifted to both higher and lower field. These shifts may again derive from the fact that the biphenyl subunit lies above the porphyrin plane. A comparison between the porphyrin dimer **3** and the monomer **1** (or the "crowned" porphyrin of Chang[9a]) reveals that the signals of the pyrrole α and β carbons have been shifted to *lower* field by ca. 8–10 ppm; no other signals are shifted by more than ca. 3 ppm.

Solid-State Structure. An X-ray structural determination of complex **21** was performed.[20] It confirmed the structure of this compound and, by extension, those of the other compounds synthesized in the course of this work. It also showed that one phenyl group of the biphenyl unit lies face to face above the porphyrin site.

Formation of the Supermolecular Species 27, 28, 31 by Binding of Organic Substrate to the Receptors 1–3. The qualitative proton

(17) (a) Kotzyba-Hibert, F.; Lehn, J. M.; Vierling, P. *Tetrahedron Lett.* **1980**, 941–944. (b) Kotzyba-Hibert, F. Ph.D. Thesis, Université Louis Pasteur de Strasbourg, 1983.

(18) Similarly, compounds **1** and **2** present *ansa*-type asymmetry which would be observable provided that the rate of ring flipping were slow on the NMR time scale.

(19) Kintzinger, J. P.; Kotzyba-Hibert, F.; Lehn, J. M.; Pagelot, A.; Saigo, K. *J. Chem. Soc., Chem. Commun.* **1981**, 833–836.

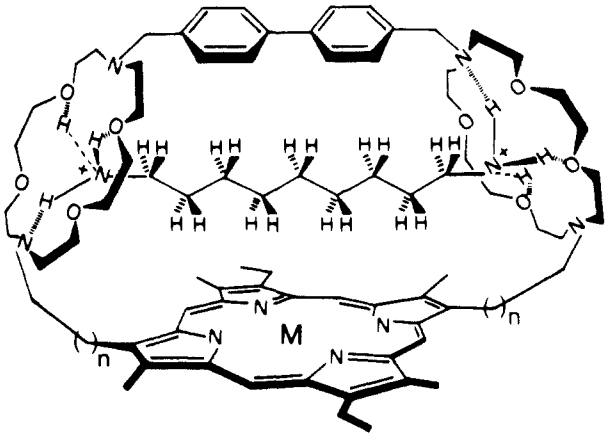
(20) Chevrier, B.; Moras, D., unpublished results.

Table III. ^{1}H NMR Chemical Shifts of the Bound ^+H_3N-$[CH_2]_n$-NH_3^+, S_n^{2+} Substrates in the Molecular Cryptates of Coreceptors **1–3** and Metalloreceptors **19**, **20**, and **22** and Chemical Shift Data for Reference Systems[a]

		substrate chemical shifts				
cryptand	substrate	α	β	γ	δ	ϵ
1	S_8^{2+}	0.60	−0.67, −1.25[c]	−1.83	−2.40	
1	S_9^{2+}	*b*	−0.08, −0.28[c]	−1.27, −1.53[c]	−2.00, −2.20[c]	−2.69
1	S_{10}^{2+}	*b*	0.4	−0.85	−1.88	−2.45, −2.99[c]
2	S_8^{2+}	*b*	*b*	*b*	−1.5	
2	S_9^{2+}	*b*	0.25	−1.03	−1.60	−2.38
2	S_{10}^{2+}	*b*	*b*	−0.62	−1.53	−2.19
3	S_8^{2+}	*b*	−0.35, −0.94[c]	−2.13, −2.57[c]	−4.53	
3	S_9^{2+}	*b*	*b*	−2.2	−4.0	−5.5
3	S_{10}^{2+}	*b*	−0.96	−2.43	−3.43	−4.75
24[d]	S_6^{2+}	*b*	0.32	0.32		
24[d]	S_7^{2+}	2.19	0.04	−0.56	0.04	
24[d]	S_8^{2+}	2.51	0.48	0.32	0.32	
26[d]	S_8^{2+}	2.78	1.50	1.34	1.34	
26[d]	S_9^{2+}	2.74	1.55	1.26	1.26	1.26
26[d]	S_{10}^{2+}	2.73	1.55	1.28	1.28	1.28
8	S_9^{2+}	1.83	3.18	3.21	3.21	3.21
19	S_8^{2+}	*b*	−0.83, −1.37[c]	−1.91	−2.43	
19	S_9^{2+}	0.32	0.02, −0.44[c]	−1.24, −1.48[c]	−2.11	−2.60
19	S_{10}^{2+}	*b*	0.42	−0.98	−1.91	−2.48, −3.00[c]
20	S_8^{2+}	*b*	*b*	−1.4	−1.6	
20	S_9^{2+}	*b*	0.28	−1.03	−1.69	−2.47
20	S_{10}^{2+}	*b*	*b*	−0.69	−1.48	−2.32
22	S_8^{2+}	−0.79	−2.31	−3.12	−4.36	
22	S_9^{2+}	−0.48	−1.64	−2.88	−4.88	−6.80
22	S_{10}^{2+}	*b*	−0.60	−2.3	−4.3	−5.3

[a] 200-MHz ^{1}H NMR spectra in CD_2Cl_2:CD_3OD 9:1 (v/v) at 18 °C. Shifts δ given vs. Me_4Si. Peak assignments were based in part on comparisons with "strapped" porphyrins[22] and by analogy to earlier work.[17,23] [b] Not assigned. Peak is not resolved or is hidden under resonances of the receptor. [c] Doublet observed. [d] 250-MHz ^{1}H NMR spectra in CD_2Cl_2:CD_3OD 9:1 (v/v) at 18 °C. Shifts δ given vs. Me_4Si. From ref 17.

NMR method described earlier[17,21] was used to study the binding of organic dications, derived from α,ω-diamines, to the receptors **1–3** and to the metalloreceptors **19**, **20**, and **22**. In general, the ^{1}H NMR spectra of the receptor in CD_2Cl_2:CD_3OD 9:1 (v/v) was recorded; slightly over 1 equiv of the appropriate diammonium dipicrate was then added and the spectrum recorded again. In



27: n = 1; M = 2H
28: n = 2; M = 2H
29: n = 1; M = Zn
30: n = 2; M = Zn

cases where substrate binding occurred, peaks ascribable to the CH_2 signals of the substrate were observed at high field, usually upfield of Me_4Si. The results of these studies are summarized in Table III. Figure 5 shows the ^{1}H NMR spectrum of the complex formed by the binding of ^+H_3N-$(CH_2)_n$-NH_3^+, n = 9 (substrate S_9^{2+}), in receptor **1**. Peaks upfield of Me_4Si are clearly visible for the β, γ, δ, and ϵ CH_2 groups of the organic substrate. No such upfield peaks are seen in the ^{1}H NMR of **1** in the absence of the substrate. Nor are they observed when S_9^{2+} is bound by 2 equiv of the dimethyl [18]-N_2O_4 macrocycle **26**[17] (Table III). In fact, as compared to this reference system, the ϵ CH_2 peak of S_9^{2+} bound to **1**, at −2.60 ppm, is shifted upfield by ca. 3.9 ppm. The upfield shifts observed here are also considerably greater than those shown by related complexes formed from **24**,[17] the bis-biphenyl bridged analogue of **1** (Table III). They may be attributed to the shielding effect of the bridging porphyrin and, to a lesser extent, of the biphenyl bridging groups. Upfield shifts are also found for various "strapped" porphyrins[22] in which an alkyl chain is covalently constained to lie above the porphyrin plane. Consequently, as with the other macrocyclic diammonium η^2-cryptates,[17,19,21,23,24] the S_9^{2+} substrate is bound as a 1:1 molecular complex within the central cavity of receptor **1** by an anchoring of the primary alkyl ammonium groups to the two [18]-N_2O_4 subunits. Structures **27–30** show a schematic representation of the supramolecular complex formed from **1** and S_9^{2+}; it is derived by analogy to earlier spectroscopic[17,19,21,23] and structural[24] studies.

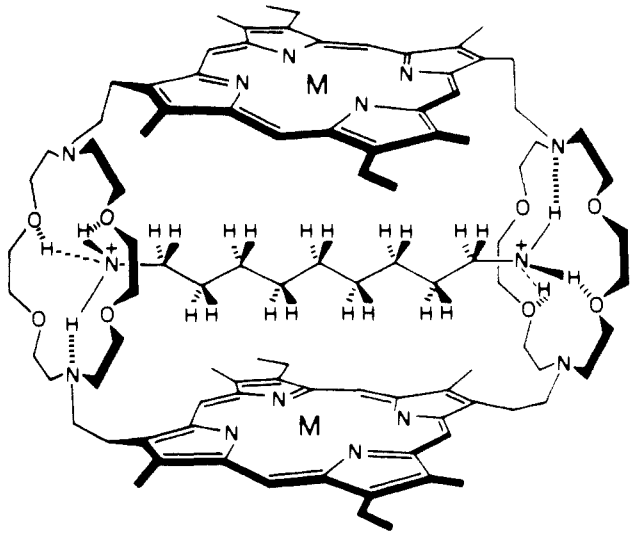
Receptor **1** similarly complexes substrates S_8^{2+} and S_{10}^{2+}. Substrates S_7^{2+} and S_{11}^{2+}, on the other hand, are not bound, and no upfield shifts are observed under the same conditions. Substrate binding to **1** is therefore selective.[17a,19,21,23,24] The *1/1 stoichiometry*

(21) See also: Jones, N. F.; Kumar, A.; Sutherland, I. O. *J. Chem. Soc., Chem. Commun.* **1981**, 990–992.

(22) (a) Wijesekera, T. P.; Paine, J. B., III; Dolphin, D.; Eisenstein, F. N. B.; Jones, T. *J. Am. Chem. Soc.* **1983**, *105*, 6747–6749. (b) Chang, C. K.; Kuo, M. S. *J. Am. Chem. Soc.* **1979**, *101*, 3413–3415. (c) Baldwin, J. E.; Klose, T.; Peters, M. *J. Chem. Soc., Chem. Commun.* **1976**, 881–883. Baldwin, J. E.; Crossley, M. J.; Klose, T.; O'Rear, E. O., III; Peters, M. K. *Tetrahedron* **1982**, *38*, 27–39. (d) Momenteau, M.; Mispelter, D.; Loock, B.; Bisagni, E. *J. Chem. Soc., Perking Trans. 1* **1983**, 189–200. (e) Ogoshi, H.; Sugimoto, H.; Yoshida, Z.-i. *Tetrahedron Lett.* **1976**, 4477–4480.

(23) Kotzyba-Hibert, F.; Lehn, J. M.; Saigo, K. *J. Am. Chem. Soc.* **1981**, *103*, 4266–4268.

(24) Pascard, C.; Riche, C.; Cesario, M.; Kotzyba-Hibert, F.; Lehn, J. M. *J. Chem. Soc., Chem. Commun.* **1982**, 557–560.



31: M = 2H
32: M = Zn

of the complexes formed was established by integration studies. Broadened signals for the substrate CH_2 protons resulted when an excess of substrate was present; apparently under these conditions, substrate not only was complexed as an η^2-cryptate but was also bound in various η^1 external orientations. So far, the relative energetics associated with these two binding modes and with the substrate binding selectivity have not been studied quantitatively.

The homologue **2** also functions as a molecular receptor. Supramolecular complexes of 1/1 stoichiometry are formed selectively with the substrates S_8^{2+}, S_9^{2+}, and S_{10}^{2+} (Table III). As with **1**, marked upfield shifts are observed, indicative of the formation of η^2-cryptates with the substrates held within the central molecular cavity (cf. structure **28**). Similar substrate binding occurs for **3** (see below).

An interesting feature of the ^1H NMR spectrum of **27** is that the β, γ, and δ CH_2 signals are split (Figure 5), reflecting the diastereotopic nature of these protons. These splittings suggest that rotation of the ^+H_3N-$(CH_2)_9$-NH_3^+ substrate about teh *N,N*-axis and/or rotation of the porphyrin subunits are/is slow. In the latter case, the supramolecular complex **27** would be seen chiral on the NMR time scale. Complexes derived from the larger homologue **2** do not show such splittings but present broad signals, suggesting that greater degrees of freedom pertain in these systems.

Formation of the Mixed Substrate Supermolecules 29, 30, 32 by Binding of Organic Substrate to the Metalloreceptors 19, 20, 22. The heterotopic apo-receptors **1** and **2** can be converted into metal-containing receptors by specifically binding a metal cation within the porphyrin ring; when Zn(II) is used, the diamagnetic complexes **19** and **20** are obtained cleanly from **1** and **2** (see above).[25] As for the free-base congeners, ^1H NMR may be used to study *organic substrate* binding to these *metalloreceptors*. Figure 6 shows the ^1H NMR spectrum of the complex which derives from the binding of S_9^{2+} into the metalloreceptor **19**. As was true for the free-base system, signals ascribable to the β, γ, δ, and ϵ CH_2 protons are observed upfield of Me_4Si, giving peaks which are not present in the absence of substrate. Upfield shifts are also displayed in complexes derived from receptor **19** and substrates S_8^{2+} and S_{10}^{2+} (but not S_7^{2+} or S_{11}^{2+}) as well as from receptor **20** and substrates S_8^{2+}, S_9^{2+}, and S_{10}^{2+} (Table III). Significantly, the complexation of molecular substrates by the metalloreceptors **19** and **20** did not result in demetalation; the visible portion of the electronic spectra was essentially identical both before and after the addition of the diammonium salts. The organic substrates are therefore bound within the central cavities of frameworks which contain bound inorganic centers. The resulting species are *organic/inorganic mixed substrate supramolecular complexes*. Structures **29** and **30** are schematic representations of the species which result when both Zn(II) and S_9^{2+} are co-complexed within the heterotopic receptors **1** and **2**.

When slightly over 1 equiv of the S_9^{2+} or S_{10}^{2+} substrate was added to either the free-base receptor **3** or its bis-zinc derivative

(25) The bis-Co^{II} complex of **3** has also been obtained recently.[27]

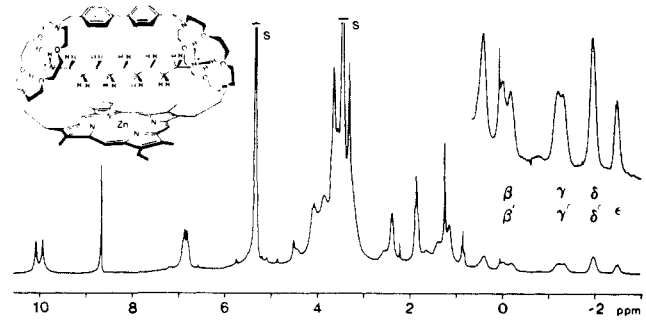


Figure 6. ^1H NMR spectrum at 200 MHz (CD_2Cl_2:CD_3OD 9:1 (v/v)) of the supramolecular complex **29** formed from the metalloreceptor **19** and the S_9^{2+} substrate ^+H_3N-$(CH_2)_9$-NH_3^+ dipicrate.

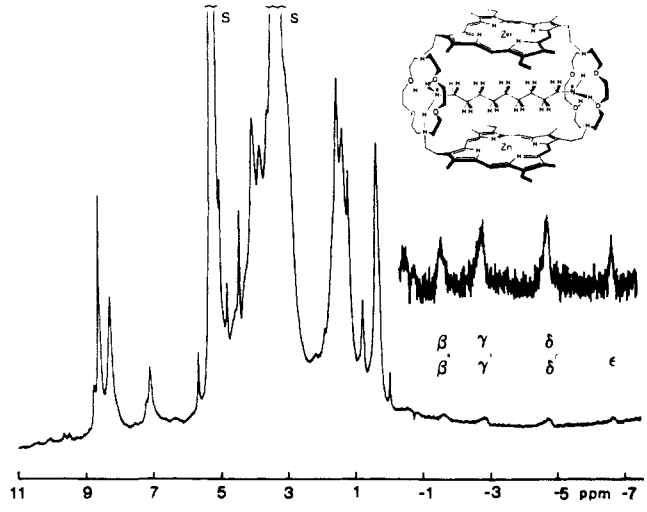


Figure 7. ^1H NMR spectrum at 200 MHz (CD_2Cl_2:CD_3OD 9:1 (v/v)) of the sparingly soluble supramolecular complex **32** formed from the metalloreceptor **22** and the S_9^{2+} substrate ^+H_3N-$(CH_2)_9$-NH_3^+ dipicrate; because of the low solubility of **32**, the spectrum also contains the signals of the metalloreceptor **22** and of uncomplexed substrate; the high-field signals (insert) are assigned to the $-CH_2-$ protons of the substrate.

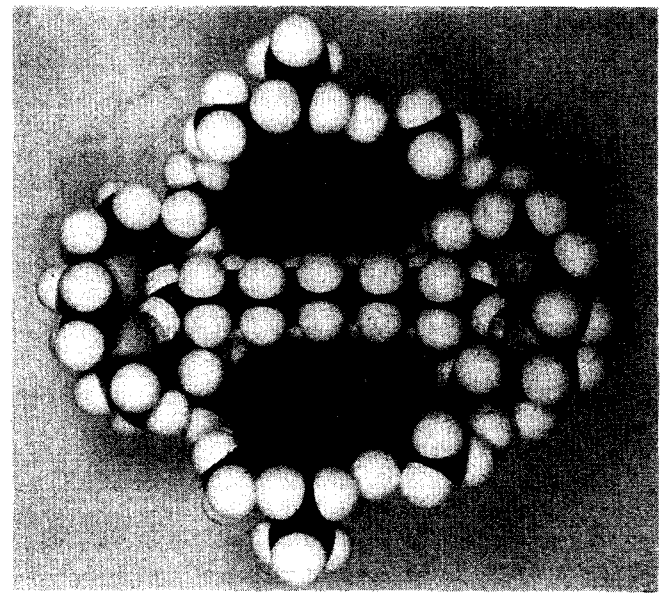


Figure 8. CPK model representation of the possible structure of the mixed substrate supramolecular species **32** formed by binding of ^+H_3N-$(CH_2)_9$-NH_3^+ to the metalloreceptor **22** (see text).

When slightly over 1 equiv of the S_9^{2+} or S_{10}^{2+} substrate was added to either the free-base receptor **3** or its bis-zinc derivative

22, complexes formed which were sparingly soluble.[26] Proton NMR analysis of these species is thus complicated by the additional presence of both free receptor and uncomplexed substrate in the solution. Since, however, only the complexed substrate displays CH_2 signals upfield of Me_4Si, the assignment of these peaks remains straightforward. As expected, the upfield shifts of the substrate CH_i signals, when bound in the porphyrin dimers **3** or **22**, are approximately twice that they are when bound in the monomers **1**, **2**, **19**, or **20** (Table III). In fact, the ϵ CH_2 protons, observed at −6.80 ppm for the complex formed from S_9^{2+} and **22** (Figure 7, Table III) are shifted by over 8 ppm as compared to the reference complex formed from **26**. Structures **31** and **32** are schematic representations of the organic/inorganic substrate supramolecular species obtained respectively from the heterotopic receptor **3** and from its Zn(II) complex **22**. The CPK molecular model shown in Figure 8 provides a possible picture of the structural features of species **32** based on present and earlier[1,17,19,24] results.

Conclusion

The results described above show that suitably designed macropolycyclic molecules function as heterotopic coreceptors allowing one to bring together within the same supramolecular structure inorganic and organic substrates complexed by means of selective subunits. Mutual interactions between the co-bound substrates should provide means for regulating the physical properties and chemical reactivity of the supramolecular species. This applies in particular to the photochemical and electrochemical properties of the complexes (such as **19–23** and **27–32**) formed by the tritopic and tetratopic receptors **1–3** described here, since these species contain photoactive and electroactive subunits; such results have been obtained and will be described in another report.[27] As pointed out earlier,[1] polytopic receptors may possess properties such as regulation, cooperativity, and allostery, which are not present in monotopic receptors. Furthermore, the ability of porphyrins to form stacking complexes with flat substrates and intercalation species with nucleic acids together with their photoactivity, confer to receptors **1–3** and to their metal complexes properties of *cyclointercalands*, potentially capable of performing photochemical reactions on selectively bound substrates, in particular photocleavage of DNA. Studies along these lines are in progress.

Experimental Section

Reagents and Solvents. All solvents and reagents were of reagent grade quality, purchased commercially, and used without further purification, except as noted below. Dichloromethane and THF were refluxed with and distilled from CaH_2 under argon. Benzene and toluene were distilled from sodium metal under argon. Pyridine was refluxed with and distilled from KOH pellets and stored over 4 Å molecular sieves under an argon atmosphere. Benzyl chloroformate was distilled at reduced pressure and stored at −70 °C. The [18]-N_2O_4 macrocycle, **12** (1,10-diaza-4,7,13,16-tetraoxacyclooctadecane), was obtained from Merck, Inc. Merck type 60 (TLC grade) silica gel or Merck activity III neutral alumina were used for column chromatography. Thin-layer chromatography was performed with commercially prepared, plastic-backed, precoated alumina or silica plates.

Physical and Spectroscopic Methods. Melting points were obtained on a Thomas-Hoover capillary apparatus and are uncorrected. Electronic spectra were recorded on either a Cary 219 or a Cary 118 spectrophotometer. Proton NMR spectra was recorded on either a Varian EM 360A (60 MHz), Bruker SY 200 (200 MHz), or Bruker WP 400 (400 MHz) spectrometer. Carbon-13 NMR spectra were recorded at 50 MHz on a Bruker SY 200 spectrometer. Chemical shifts are reported in ppm vs. Me_4Si. Mass spectrometry was performed either by Chemical Ionization at the Laboratoire de Spectrométrie de Masse, Strasbourg, or by Fast Atom Bombardment at the Service Central de Microanalyse du CNRS, Lyon. Microanalyses were obtained at the Centre de Microanalyses du CNRS, Institut de Chimie de Strasbourg.

Techniques for Handling Unstable Compounds. The free-base porphyrins were treated as if light sensitive and handled in subdued light since similar porphyrinic compounds have been reported to be light sensitive.[10,15,16] The final tetraamine products **1–3** were stored under argon.

Biphenyl-Bridged Bis-[18]-N_2O_4 Macrocycle 9. Direct Procedure. To a solution of the [18]-N_2O_4 macrocycle **12** (3 g, 11.5 mmol) and triethylamine (3 mL) in CH_2Cl_2 (25 mL), a solution of 4,4′-dichloroformylbiphenyl (**13**) (1 g, 3.57 mmol) in CH_2Cl_2 (100 mL) was added dropwise over 2 h with vigorous stirring. The mixture was stirred for an additional 16 h. Toluene (50 mL) was then added, and the solution was reduced in volume to 50 mL on a rotary evaporator. The organic solution was extracted with three 100-mL portions of water. The aqueous washings were combined and extracted with CH_2Cl_2 (3 × 100 mL). The dichloromethane solutions were combined, dried over Na_2SO_4, and evaporated to dryness to yield the diamine diamide **9** as an oil (2.2 g, 85% based on **13**). Drying the original toluene solution over Na_2SO_4 and evaporation of the solvent afforded the macrotricyclic tetraamide **25** (0.43 g).[17] Basification of the final aqueous phase to pH 10 with 50% aqueous NaOH, extraction into CH_2Cl_2, drying with $MgSO_4$, and evaporation gave the starting [18]-N_2O_4 compound **12** (0.52 g). For compound **9**: ^1H NMR ($CDCl_3$) 2.85 (m, 8 H, CH_2–NH), 3.20 (m, 2 H, N*H*), 3.70 (m, 40 H, CH_2–O, CH_2–NCO), 7.60 (dd, J = 14, 10 Hz, 8 H, aromatic H).

Biphenyl-Bridged Bis[18]-N_2O_4 Macrocycle 9. Indirect Procedure. Step 1, Preparation of 15. To a solution of 4,4′-dichloroformylbiphenyl (0.37 g, 1.32 mmol) in CH_2Cl_2 (30 mL) was added a solution f the *N*-benzyloylcarbonyl monoprotected [18]-N_2O_4 macrocycle **14**[12] (1.04 g, 2.62 mmol) in CH_2Cl_2 (60 mL) and triethylamine (0.36 mL) over a period of 4 h with vigorous stirring. After the reaction mixture was washed with 100 mL of 10% aqueous NaOH, the organic layer was dried over Na_2SO_4 and evaporated to dryness to yield the diprotected diamide **15** as an oil (1.31 g, quantitative). This product was used directly without further purification. ^1H NMR ($CDCl_3$) 3.62 (m, 48 H, CH_2–O, CH_2–N), 5.11 (s, 4 H, Ar–CH_2), 7.40 (m, 18 H, aromatic H). **Step 2, Preparation of 9.** The diprotected diamide **15** (1.31 g, 1.31 mmol) in CH_3OH (150 mL) and palladium on carbon catalyst (5%, 0.2 g) were stirred under hydrogen overnight, or until no further hydrogen uptake was observed. The reaction mixture was filtered through Celite and evaporated to dryness. The crude product was dissolved in CH_2Cl_2:CH_3OH 1:1 (v/v) and subject to a second filtration through a small plug of alumina. The diamide diamine **9**, identical to that obtained above, was isolated as an oil (0.95 g, quantitative).

Biphenyl-C_2-porphyrin Bis-[18]-N_2O_4 Macrocyclic Tetraamide 10. Dry pyridine (600 mL) was placed in a 1 L round-bottomed flask equipped with a Vigreux column and an argon inlet, and the column was warmed to 55 °C. Solutions of the *p*-nitrophenyl ester 6[10] (336 mg, 0.43 mmol) and diamide diamine **9** (292 mg, 0.40 mmol) in dry pyridine (50 mL each) were made up and quickly poured into the warm pyridine. The reaction was stirred for 2 days at 55 °C under argon in the dark. The pyridine was then removed in vacuo, and the residue was taken up in $CHCl_3$ and washed with 5% aqueous NaOH to remove *p*-nitrophenol. The aqueous phase was further extracted with $CHCl_3$ (3 × 100 mL). The combined $CHCl_3$ solutions were dried over Na_2SO_4, and the solvent was removed on a rotary evaporator to yield the crude product, which is contaminated with an unidentified porphyrinic impurity of lower R_f (silica, 5% CH_3OH in $CHCl_3$ eluent). It is nonetheless of sufficient purity that it may be used directly for the next step. When necessary, chromatography was carried out on a 1.5 × 40 cm column of silica gel with 2.5% CH_3OH in CH_2Cl_2 as the eluent. The first major band was collected and recrystallized from CH_2Cl_2–hexane to yield 285 mg (54.6%) of the analytically pure tetraamide **10**. ^{13}C NMR ($CDCl_3$): 11.3, 11.9 (porphyrin–CH_3), 17.4 (CH_2–CH_3), 19.6 (CH_2–CH_3), 34.8 (CH_2–CO), 49.4, 49.7 (N–CH_2–CH_2–O), 70.2, 70.5, 70.8, 71.0 (N–C-H_2–CH_2–O), 96.3, 97.6 (meso C), 126.6, 126.8, (biphenyl C_2, C_3, C_5, C_6) 133.9, 134.6, 135.4, 138.7 (pyrrole β C), 138.4, 139.3, 149.1, 149.9 (pyrrole α C), 140.2, 140.4 (biphenyl C_1, C_4) 171.3, 172.3 (CO). Anal. Calcd for $C_{70}H_{88}N_8O_{12}$: C, 68.16; H, 7.19; N, 9.08. Found: C, 68.19; H, 7.31; N, 8.83. *m/e* 1233 (calcd 1233).

Biphenyl-C_3-porphyrin Bis-[18]-N_2O_4 Macrocyclic Tetraamide 11 was prepared in 50% yield from the *p*-nitrophenyl ester 7[10] (261.8 mg, 0.32 mmol) and the diamine diamide 9 (251.7 mg, 0.34 mmol) with use of the same synthesis and purification procedure as above. Again, the crude product was generally sufficiently pure to be used directly for further work. m/e 1261 (calcd 1261).

Biphenyl-C_2-porphyrin Bis-[18]-N_2O_4 Macrocyclic Tetraamine 1. The crude tetraamide **10** (165 mg, 0.13 mmol) was dissolved in 80 mL of boiling CH_2Cl_2. A solution of zinc acetate (0.5 g) in CH_3OH (10 mL) was then added, and the mixture was stirred at 40 °C for 5 min. At this

(26) When substrate S_8^{2+} for which appreciable but not optimal binding is to be expected (Table III) is added to either **3** or **22**, complexes are obtained which are significantly more soluble than those obtained with S_9^{2+} or S_{10}^{2+}. With either the S_7^{2+} or S_{11}^{2+} substrates there is no evidence of complexation and the solution remains free of precipitate.

(27) Gubelmann, M.; Lehn, J. M., unpublished results.

point it was confirmed by visible spectroscopy that the zinc insertion was complete (only bands at 537 and 575 nm were observed in the 700–450-nm range). The reaction mixture was then poured into 100 mL of H_2O. The organic layer was separated off, and the aqueous layer was washed with more CH_2Cl_2 (3 × 30 mL). The organic layers were combined, dried over Na_2SO_4, and evaporated to dryness. After being flushed with argon, the red residue was treated with diborane (30 mL of a 1 N solution in THF) and heated at reflux for 1 h. After the mixture was cooled, H_2O was added to quench the excess diborane and the solution was taken to dryness on a rotary evaporator. The solids were treated with 8 N HCl, and the resulting solution was heated for 8 h at reflux. After being allowed to cool, the solution was made basic by the addition of 1 N aqueous LiOH and extracted with CH_2Cl_2 (3 × 50 mL). The CH_2Cl_2 extracts were combined, dried over $MgSO_4$, and evaporated to dryness. The crude yield was virtually quantitative. Purification involved chromatography on alumina (1.5 × 40 cm column) with 2.75% CH_3OH in CH_2Cl_2 as the eluent. Collection of the major band followed by recrystallization from CH_2Cl_2–hexane yielded 115 mg (73% based on **10**, 54% based on **9**) of the analytically pure tetraamine **1**. ^1H NMR ($CDCl_3$): −3.75 (s, 2 H, pyrrole), 1.79 (br, 8 H, macrocyclic N–CH_2), 1.82 (t, 6 H, CH_2–CH_3), 2.18 (br, 4 H, N–CH_2–biphenyl), 2.85 (br, 8 H, macrocyclic N–CH_2), 3.25 (br, 16 H, macrocyclic O–CH_2), 3.54 (s, 12 H, CH_3), 3.59 (br, 4 H, N–CH_2–CH_2–porphyrin), 3.61 (s, 8 H, macrocyclic O–CH_2), 3.86 (t, 8 H, macrocyclic O–CH_2), 4.11 (q, 4 H, CH_2–CH_3), 4.22 (br, 4 H, N–CH_2–CH_2–porphyrin), 5.90 (br, 4 H, aromatic H), 6.41 (d, 4 H, aromatic H), 10.02 (s, 2 H, meso H), 10.09 (s, 2 H, meso H). ^{13}C NMR ($CDCl_3$): 11.6, 12.0 (CH_3), 17.6 (CH_2–CH_3), 19.6 (CH_2–CH_3), 24.4 (porphyrin–CH_2–CH_2), 52.6, 54.0 (N–CH_2–CH_2–O), 56.0 (porphyrin–CH_2–CH_2–N), 57.2 (biphenyl–CH_2–N), 68.0, 69.2, 69.3, 70.0 (N–CH_2–CH_2–O), 94.8, 95.2 (meso C), 123.6, 136.4 (biphenyl C_2, C_3, C_5, C_6), 124.0, 127.0 (pyrrole β C), 132.8, 134.3, 136.7, 139.8 (pyrrole α C), 135.6, 136.0 (biphenyl C_1, C_4). λ_{max} 397 nm. Anal. Calcd for $C_{70}H_{96}N_8O_8$: C, 71.39; H, 8.22; N, 9.52. Found: C, 71.13; H, 8.14; N, 9.37. *m/e* 1177 (calcd 1177).

Biphenyl-C_3-porphyrin Bis-[18]-N_2O_4 Macrocyclic Tetraamine 2. With use of the same procedure, the tetraamide **11** was reduced to the tetraamine **2**. Purified **11** (550 mg, 0.44 mmol) gave analytically pure **2** (480 mg) in 91% yield after chromatography and recrystallization as above. ^1H NMR ($CDCl_3$): −3.69 (s, 2 H, pyrrole), 1.82 (t, 6 H, CH_2–CH_3), 2.06 (br, 8 H, macrocyclic N–CH_2), 2.53 (m, 4 H, CH_2–CH_2–CH_2), 2.78 (s, 4 H, N–CH_2–biphenyl), 2.85 (br, 8 H, macrocyclic N–CH_2), 3.01 (br, 8 H, macrocyclic O–CH_2), 3.25 (br, 8 H, macrocyclic eo–CH_2), 3.46 (br, 8 H, macrocyclic O–CH_2), 3.53 (m, 4 H, CH_2–CH_2–CH_2–N), 3.61 (t, 8 H, macrocyclic O–CH_2), 3.62 (s, 6 H, CH_3), 3.64 (s, 6 H, CH_3), 4.05 (q, 4 H, CH_2–CH_3), 4.15 (t, 4 H, porphyrin–CH_2–CH_2–CH_2), 6.41 (m, 4 H, aromatic H), 6.66 (d, 4 H, aromatic H), 10.06 (s, 2 H, meso H), 10.13 (s, 2 H, meso H). ^{13}C NMR ($CDCl_3$): 11.7, 12.1 (CH_3), 17.8 (CH_2–CH_3), 20.0 (CH_2–CH_3), 24.7 (porphyrin–CH_2–CH_2–CH_2), 31.3 (CH_2–CH_2–CH_2), 53.9, 54.8 (N–CH_2–CH_2–O), 56.0 (CH_2–CH_2–CH_2–N), 59.1 (biphenyl–CH_2–N), 69.6, 70.4, 70.6, 71.0 (N–$CH_2$$CH_2$–O), 96.5, 96.8 (meso C), 125.9, 128.6 (biphenyl C_2, C_3, C_5, C_6), 126.9, 129.4 (pyrrole β C), 135.2, 135.9, 140.7, 142.3 (pyrrole α C), 138.1, 138.7 (biphenyl C_1, C_4). λ_{max} 397 nm. Anal. Calcd for $C_{72}H_{100}N_8O_8$: C, 71.73; H, 9.29; N, 8.36. Found: C, 71.66; H, 9.10; N, 8.22.

Bis-C_2-porphyrin Bis-[18]-N_2O_4 Macrocyclic Tetraamide 16. Direct Procedure. The *p*-nitrophenyl ester **6**[10] (83.9 mg, 1.1 mmol) and the [18]-N_2O_4 macrocycle **12** (26.3 mg, 1.0 mmol) were heated together for 48 h in pyridine (200 mL) at 55 °C in the dark under argon. The pyridine was then removed in vacuo, and the residues were taken up in $CHCl_3$ (ca. 400 mL) and washed with 5% aqueous NaOH. After being dried over Na_2SO_4, the solvent was removed on a rotary evaporator to yield the very crude tetraamide product. Chromatography on TLC grade silica (1.5 × 40 cm column) eluting with 2.75% CH_3OH in $CHCl_3$ gave, after collection of the first major band and subsequent recrystallization from CH_2Cl_2–hexane, the purified tetraamide **16** (10 mg, 12%). *m/e* 1529 (calcd 1529).

C_2-Porphyrin-Bridged Bis-(M-CBz protected [18]-N_2O_4) Macrocycle 17. The C_2 *p*-nitrophenyl ester **6**[10] (233 mg, 0.30 mmol) and the monoprotected [18]-N_2O_4 macroycycle **14**[12] (236 mg, 0.60 mmol) were added to 400 mL of dry pyridine and stirred for 48 h at 55 °C in the dark under an argon atmosphere. The pyridine was then removed in vacuo, and the residue was taken up in $CHCl_3$ and washed with 5% aqueous NaOH. After being dried over Na_2SO_4 and evaporated to dryness on a rotary evaporatory, the crude product was purified by chromatography on TLC grade silica with first 1% CH_3OH in CH_2Cl_2 and then 2% CH_3OH in CH_2Cl_2 as eluents. The major band was collected and recrystallized from CH_2Cl_2–hexane to yield the analytically pure product **17** (250 mg, 66%). ^1H NMR ($CDCl_3$): 1.85 (t, 6 H, CH_2–CH_3), 3.09 (m, 8 H, macrocyclic CH_2), 3.21 (m, 8 H, macrocyclic CH_2), 3.28 (s, 6 H, CH_3), 3.29 (s, 6 H, CH_3), 3.33 (m, 8 H, macrocyclic CH_2), 3.39 (m, 8 H, macrocyclic CH_2), 3.64 (m, 16 H, macrocyclic O–CH_2), 3.94 (br, 4 H, CH_2–CON), 4.15 (q, 4 H, CH_2–CH_3), 5.13 (s, 4 H, O–CH_2–phenyl), 7.38 (s, 10 H, aromatic H), 10.12 (s, 2 H, meso H), 10.46 (s, 2 H, meso H). (No peaks ascribable to the pyrrole N–H signal were observed for this compound.) Anal. Calcd for $C_{72}H_{94}N_8O_{14}$: C, 66.75; H, 7.31; N, 8.64. Found: C, 66.36; H, 7.22; N, 8.50.

C_2-Porphyrin-Bridged Bis-[18]-N_2O_4 Macrocyclic Diamine Diamide 18. The diprotected porphyrin-bridged compound **17** (400 mg, 0.31 mmol) was dissolved at room temperature in 10 mL of concentrated HCl. If necessary, trifluoroacetic acid (ca. 5 mL) was then added to solubilize the porphyrin. The solution was stirred for several hours while the progress of the reaction was closely monitored by TLC. This was done by removing small aliquots from the reaction mixture, basifying with aqueous LiOH, extracting into $CHCl_3$, and drying over $MgSO_4$. When the spot at R_f 0.30 became dominant (and before spots with lower R_f values began to appear), the reaction was quenched by the slow addition of 1 N aqueous LiOH. After the solution had reached pH 10, it was extracted with $CHCl_3$ (3 × 100 mL). The $CHCl_3$ extracts were combined, dried over $MgSO_4$, and taken to dryness in vacuo to yield 313 mg (98%) of the crude diamine diamide **18**. In general, the crude material is of sufficient purity that it may be used directly in the subsequent macrocycle forming reaction. As necessary, however, chromatography on activity III alumina, with 1% CH_3OH in $CHCl_3$, as eluent, was used to obtain pure material. ^1H NMR ($CDCl_3$): −3.81 (s, 2 H, pyrrole), 1.87 (t, 6 H, CH_2–CH_3), 1.99 (s, 2 H, macrocyclic NH), 2.34 (m, 8 H, macrocyclic N–CH_2), 2.96 (s, 8 H, macrocyclic CH_2), 3.08 (m, 8 H, macrocyclic CH_2), 3.29 (s, 6 H, CH_3), 3.30 (s, 6 H, CH_3), 3.42 (s, 8 H, macrocyclic CH_2), 3.64 (t, 16 H, macrocyclic O–CH_2), 3.93 (m, 4 H, CH_2–CON), 4.15 (q, 4 H, CH_2–CH_3), 10.01 (s, 2 H, meso H), 10.38 (s, 2 H, meso H). ^{13}C NMR ($CDCl_3$): 12.2, 13.2 (CH_3), 18.7 (CH_2–CH_3), 21.1 (CH_2–CH_3), 35.44 (CH_2–CON), 47.8, 50.1 (N–CH_2–CH_2–O), 70.7, 71.3, 71.4 (N–CH_2–CH_2–O), 97.5, 98.7, (meso C), 134.8, 135.6, 139.6, 141.4 (pyrrole β C), 145.4, 147.2, 149.2, 150.8 (pyrrole α C), 171.1 (CO). Anal. Calcd for $C_{56}H_{82}N_8O_{10}\cdot 1.5H_2O$: C, 63.97; H, 7.86; N, 10.65. Found: C, 63.90; H, 7.90; N, 10.56. *m/e* 1026 (calcd 1026).

Bis-C_2-porphyrin Bis-[18]-N_2O_4 Macropentacyclic Tetraamide 16. Stepwise Procedure. The diamine diamide **18** (138 mg, 0.11 mmol) was mixed with the *p*-nitrophenyl ester **6** (110 mg, 0.11 mmol) in pyridine (300 mL) and stirred for 48 h at 55 °C in the dark under an argon atmosphere. The pyridine was then removed in vacuo, and the residue was taken up in $CHCl_3$ (300 mL). After being washed with 1 N aqueous LiOH (2 × 100 mL), the organic phase was dried over Na_2SO_4 and taken to dryness on a rotary evaporator to yield the crude tetraamide **16** (93 mg, 45%). The major migrating spot of this crude product proved by TLC (silica, 5% CH_3OH in $CHCl_3$) to be identical with the purified macrocyclic material obtained by the direct procedure. A small scale chromatographic separation (silica, 2.75% CH_3OH in $CHCl_3$ eluent) yielded purified tetraamide **16** identical with that prepared by the direct procedure. *m/e* 1529 (calcd 1529).

Bis-C_2-porphyrin Bis-[18]-N_2O_4 Macropentacyclic Tetraamine (3). The crude tetraamide **16** (180 mg, 0.12 mmol), prepared from **18**, was dissolved in 100 mL of $CHCl_3$, and a solution of 0.5 g of zinc acetate in CH_3OH (10 mL) was added. The solution was heated at reflux for 0.5 h, the resulting pink solution was poured into H_2O, and the metalloporphyrin complex was extracted into $CHCl_3$. After the organic phase was dried over Na_2SO_4, the solvent was removed in vacuo and the flask was flushed with argon. Diborane (25 mL of a 1 N solution in THF) was added, and the resulting solution was heated at reflux for 8 h. After the mixture was cooled, excess diborane was quenched cautiously with water. The reaction mixture was then taken to dryness on a rotary evaporator. Aqueous 8 N hydrochloric acid (50 mL) was added to the solid residue, and the resulting mixture was heated at reflux for 8 h. After being cooled, the solution was made basic to pH 10 or 11 by the addition of 1 N aqueous LiOH and extracted with $CHCl_3$ (3 × 100 mL). The organic extracts were combined, dried over $MgSO_4$, and taken to dryness on a rotary evaporator. The resulting crude product was chromatographed on alumina, eluting with 1% CH_3OH in $CHCl_3$, to yield, after recrystallization from CH_2Cl_2–hexane, 150 mg of the tetraamine **3** (86.5% based on **16**, 25% based on **6**). By the same procedure, compound **3** can also be prepared in 10% yield (based on **6**) from the crude tetraamide **16** obtained by the direct condensation procedure. In this case, at least two chromatographic separations on alumina are required before pure product is obtained. ^1H NMR ($CDCl_3$): −4.39 (s, 4 H, pyrrole), 1.71 (br, 8 H, N–CH_2–CH_2–porphyrin), 1.90 (t, 12 H, CH_2–CH_3), 2.25 (br, 16 H, macrocyclic N–CH_2), 2.72 (br, 8 H, N–CH_2–CH_2–porphyrin), 2.85 (s, 12 H, CH_3), 3.04 (s, 12 H, CH_3), 3.45 (br, 16 H, macrocyclic O–CH_2), 3.59 (s, 16 H, macrocyclic O–CH_2), 4.10 (q, 8 H, CH_2–CH_3), 8.30 (br, 4 H, meso H), 9.76 (s, 4 H, meso H). ^{13}C NMR ($CDCl_3$): 10.9, 11.1 (CH_3), 17.9 (CH_2–CH_3), 20.1 (porphyrin–CH_2–CH_3), 21.3 (porphyrin–CH_2–CH_2–N), 53.6 (N–CH_2–CH_2–O),

55.8 (porphyrin-CH_2-CH_2-N), 70.8, 71.2 (N-CH_2-CH_2O), 95.5, 95.7 (meso C), 134.3, 135.2, 136.8, 141.9 (pyrrole β C), 143.0, 145.1 (pyrrole α C). λ_{max} 388 nm. Anal. Calcd for $C_{88}H_{120}N_{12}O_8$: C, 71.71; H, 8.21; N, 11.40. Found: C, 71.90; H, 8.12; N, 11.39. *m/e* 1473 (calcd 1473).

Zn Biphenyl-C_2-porphyrin Bis-[18]-N_2O_4 Macrotetracyclic Complex 19. The free-base porphyrin **1** (10 mg, 0.0085 mmol) was dissolved in 10 mL of hot CH_2Cl_2, and 0.89 mL of a 0.010 N solution of zinc acetate in CH_3OH was added. When, as judged by the absence of bands at 497 *nm* 619 nm in the visible spectrum, the reaction was considered complete, the pink solution was poured into a very dilute aqueous solution of LiOH. The organic layer was separated off, and the aqueous phase was extracted with $CHCl_3$ (2 × 20 mL). The organic phases were combined, dried over $MgSO_4$, and taken to dryness in vacuo to yield **19** (10.2 mg, 97%). ^1H NMR ($CDCl_3$): no peaks associated with the pyrrole N-H protons are observed; other features were similar to those observed for the free-base **1**. λ_{max} 405 nm.

Zn Biphenyl-C_3-porphyrin Bis-[18]-N_2O_4 Macrotetracyclic Complex 20 was prepared from **2** by the same procedure used to prepare **19** from **1**. For 10 mg (0.0083 mmol) of the free-base, 0.90 mL of the stock 0.010 N zinc acetate solution was used to give 10 mg (95%) of the zinc complex **20**. ^1H NMR ($CDCl_3$): no signals ascribable to a pyrrolic N-H are detected; other features much as for the free-base. λ_{max} 402 nm.

Zn_2 Bis-C_2-porphyrin Bis-[18]-N_2O_4 Dinuclear Macropentacyclic Complex 22 was prepared in 97% yield from **3** by using a similar procedure. For 10 mg of the free-base **3**, 1.42 mL of the 0.010 N zinc acetate stock solution was used to give 10.5 mg of the bis-zinc complex **22**. ^1H NMR ($CDCl_3$): no signals ascribable to a pyrrolic N-H were observed; other features much as for the free-base. λ_{max} 385 nm.

Cu Biphenyl-C_2-porphyrin Bis-[18]-N_2O_4 Macrotetracyclic Complex 21. The purified free-base compound, **1** (50 mg, 0.043 mmol), was dissolved in $CHCl_3$ (20 mL) at 40 °C, and 5 mL of a saturated solution of copper acetate in CH_3OH were added. After approximately 10 min, when visible spectroscopy indicated the absence of starting material (no bands were observed at 497 and 619 nm), the reaction mixture was poured into a 0.1 N aqueous solution of NaCN, made slightly basic by the addition of LiOH. The organic layer was extracted out, washed with water (3 × 20 mL), dried over Na_2SO_4, and stripped to dryness on a rotary evaporator. Recrystallization from CH_2Cl_2-hexane yielded the copper complex **21** as large purple crystals (50 mg, 95%). λ_{max} 399 nm. Anal. Calcd for $C_{70}H_{99}N_8O_8Cu \cdot 2H_2O$: C, 65.94; H, 7.75. Found: C, 66.24; H, 7.81. This compound was also characterized by an X-ray crystallographic structure determination.[20]

Cu_2 Bis-C_2-porphyrin Bis-[18]-N_2O_4 Dinuclear Macropentacyclic Complex 23 was prepared in an identical manner as above from the free-base **3** in 92% yield. λ_{max} 390 nm. The crystals obtained were kept in view of an X-ray crystallographic analysis. Anal. Calcd for $C_{88}H_{116}N_{12}O_8Cu_2 \cdot 5H_2O$: C, 62.65; H, 7.53; N, 9.96. Found: C, 62.69; H, 7.22; N, 9.62.

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Registry No. 1, 90633-79-7; **1**·$^+H_3N(CH_2)_8NH_3^+$, 103201-89-4; **1**·$^+H_3N(CH_2)_9NH_3^+$, 90633-81-1; **1**·$^+H_3N(CH_2)_{10}NH_3^+$, 103201-90-7; **2**, 90633-80-0; **2**·$^+H_3N(CH_2)_8NH_3^+$, 103201-91-8; **2**·$^+H_3N(CH_2)_9NH_3^+$, 90633-82-2; **2**·$^+H_3N(CH_2)_{10}NH_3^+$, 103201-92-9; **3**, 90653-21-7; **3**·$^+H_3N(CH_2)_8NH_3^+$, 103201-93-0; **3**·$^+H_3N(CH_2)_9NH_3^+$, 90653-22-8; **3**·$^+H_3N(CH_2)_{10}NH_3^+$, 103201-94-1; **6**, 74427-71-7; **9**, 90653-18-2; **10**, 90633-76-4; **10** (Zn complex), 103201-95-2; **11**, 90633-77-5; **12**, 23978-55-4; **13**, 2351-37-3; **14**, 42031-79-8; **15**, 90633-73-1; **16**, 90653-20-6; **16** (Zn complex), 103201-96-3; **17**, 90633-78-6; **18**, 90653-19-3; **19**, 90603-80-8; **19**·$^+H_3N(CH_2)_8NH_3^+$, 90818-88-5; **19**·$^+H_3N(CH_2)_9NH_3^+$, 90818-90-9; **19**·$^+H_3N(CH_2)_{10}NH_3^+$, 90818-89-5; **20**, 90603-81-9; **20**·$^+H_3N(CH_2)_8NH_3^+$, 90822-43-8; **20**·$^+H_3N(CH_2)_9NH_3^+$, 90818-90-9; **20**·$^+H_3N(CH_2)_{10}NH_3^+$, 90818-91-8; **21**, 103201-97-4; **22**, 90603-82-0; **22**·$^+H_3N(CH_2)_8NH_3^+$, 90818-92-1; **22**·$^+H_3N(CH_2)_9NH_3^+$, 90818-93-2; **22**·$^+H_3N(CH_2)_{10}NH_3^+$, 90818-94-3; **23**, 103201-98-5; $^+H_3N(CH_2)_8NH_3^+$, 49745-06-4; $^+H_3N(CH_2)_9NH_3^+$, 103201-88-3; $^+H_3N(CH_2)_{10}NH_3^+$, 49745-07-5.

The Mechanism of Nickel-Catalyzed Ethylene Hydrocyanation. Reductive Elimination by an Associative Process

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Abstract: The complex $(C_2H_4)L(CN)(C_2H_5)Ni^{II}$ [L = P(O-*o*-tolyl)$_3$] has been identified at −40 °C by ^1H, ^{31}P, and ^{13}C NMR spectroscopy as the primary intermediate in the catalytic hydrocyanation of ethylene. Reaction of this intermediate with L causes reductive elimination of propanenitrile and produces $(C_2H_4)L_2Ni$ which reacts with ethylene and hydrogen cyanide to regenerate the intermediate. Measurements of second-order rate constants at −50 to −10 °C result in $\Delta H^\ddagger$ = 8.8 ± 0.9 kcal/mol and $\Delta S^\ddagger$ = −34 ± 4 eu ($\Delta G^\ddagger$ = 16.7 ± 0.1 kcal/mol at −40 °C). At higher L concentrations, these nickel species are also in equilibrium with $(C_2H_4)L_3Ni$, L_4Ni, and $HNi(CN)L_3$ which remove nickel from the productive catalytic cycle. Equilibrium constants relating these species and corresponding thermodynamic parameters have been determined. The rates of dissociation of L from L_4Ni and $HNi(CN)L_3$ have also been determined. The former reaction is very slow with $\Delta H^\ddagger$ = 20.1 ± 1.6 kcal/mol and $\Delta S^\ddagger$ = 7 ± 7 eu ($\Delta G^\ddagger$ = 18.5 kcal/mol at −40 °C) whereas the latter is about 10^3 faster with $\Delta H^\ddagger$ = 18.8 ± 2.7 kcal/mol and $\Delta S^\ddagger$ = 17 ± 10 eu ($\Delta G^\ddagger$ = 14.8 kcal/mol at −40 °C).

The development of the Du Pont adiponitrile process,[1] i.e., the dihydrocyanation of butadiene, has provided on the one hand a remarkable example of industrial application of homogeneous catalysis and on the other an excellent opportunity for detailed mechanistic studies of a complex practical system. A series of recent reports from our laboratories,[2-11] as well as others,[12-17] is developing a general picture of nickel-catalyzed olefin hydrocyanation.[18,19] However, understanding of many of the funda-

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