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Dimeric Mn(III)-Tetraarylporphyrins as Catalysts for H_2O_2-Promoted Olefin Epoxidation.

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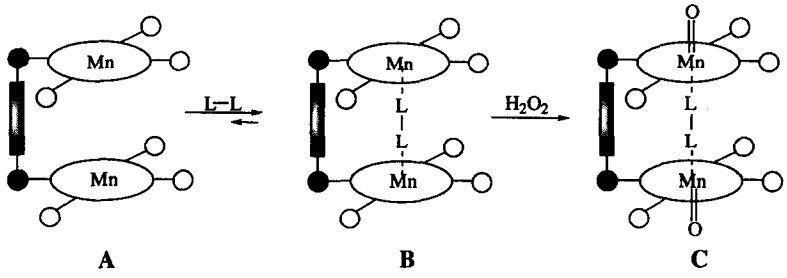
Abstract: The first example of dimeric Mn(III)-tetraarylporphyrins able to catalyze olefin epoxidation is reported. In the presence of one equivalent of lipophilic bidentate ligand **3** the efficiency of some of these catalysts is among the highest reported to now in 30% H_2O_2-promoted epoxidation (up to 1500 overall catalytic cycles). Slightly better results were obtained replacing **3** with two equivalents of N-hexylimidazole **10**.

Since the early 70's a great number of dimeric metalloporphyrins in which two identical or different moieties are covalently linked through one or more bridges have been synthesized.[1,2] They have found application as models of important biological systems, for instance the photosynthetic reaction centres of plants and bacteria ,[3] as well as as catalysts for the electrochemical dioxygen [4] or proton reduction [5]. The selective binding of host molecules inside the cavity determined by the relative orientation of the two metalloporphyrin halves allowed the creation of artificial allosteric systems,[6] the design of ditopic molecular receptors [7] and the template synthesis of cyclic porphyrin oligomers [8]. Despite their versatility, illustrated by these few examples, and though metalloporphyrin catalyzed hydrocarbon oxygenations represent a very active field of research,[9] no attempt to use dimeric complexes for this purpose has been reported. Unstability under oxidative conditions and the rather elaborated synthesis of most dimeric metalloporphyrins can explain this apparent paradox.

We are currently interested in the design of efficient catalytic systems for hydrogen peroxide hydrocarbon oxygenation based on Mn(III)-tetraarylporphyrins. Some years ago we recognized the basic features for the stability of the catalyst under oxidative conditions;[10] we also pointed out that the degradation of the heterocyclic nitrogen bases added as co-catalysts is a major drawback for the efficiency of the whole system.[11] Pyridine or imidazole derivatives acting as axial ligands for the metal centre promote the formation of a high valent Mn-oxo species, which is the oxidizing intermediate in the catalytic cycle;[12] their presence provides increased reaction rates and higher degrees of regio- and stereoselectivity.[13] However the progressive destruction of the ligand hampers the catalytic activity, determining its definitive end, even if the structure of the metalloporphyrin is still apparently unaltered. We previously faced this problem by covalently linking an imidazole or pyridine residue to the macrocyclic ring. The consequent entropically enhanced coordination of the ligand to the metal centre does improve the catalytic efficiency of the system, both in terms of reaction rates and stability.[14] Looking for an alternative approach, we turned our attention to some appealing findings in the field of dimeric metalloporphyrin chemistry.

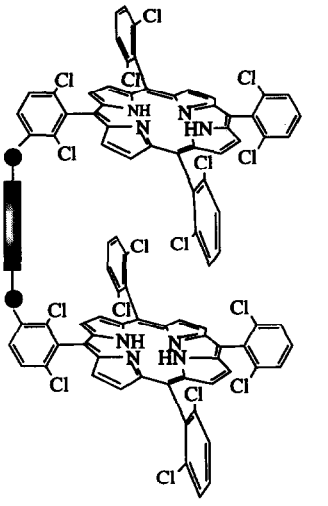
In the presence of H_2O_2 and N-methylimidazole, cofacial dimeric Mn(III)-porphyrins form high valent Mn-oxo species.[15] The close proximity of the two porphyrin moieties imposed by means of a single rigid spacer prevents the entrance of N-methylimidazole into the cavity, and the coordination of one molecule of ligand to each Mn ion occurs on the external faces of the dimer. A different coordination behaviour was reported for singly bridged dimeric Mn(II)- and Fe(II)-tetraarylporphyrins able to assume more open configurations, that form stable 1/1 adducts with bidentate nitrogen bases of appropriate size and shape.[16,17] In this case entropic factors favor the inclusion of the ligand within the cavity determined by a clamshell configuration of the dimeric porphyrin and cause very high values of the overall binding constants. Therefore, dimeric Mn(III)-tetraaryl-porphyrin (**A**, Scheme 1) able to form an inclusion complex (**B**) should meet the requirement of a strong interaction between the ligand and the metal. Moreover in the presence of H_2O_2 the access of the oxidizing high valent Mn-oxo species (**C**) to the coordinated ligand should be sterically prevented. We describe here the first attempt to build an efficient catalytic system based on these premises.

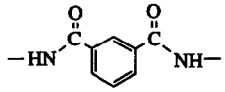
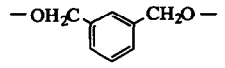
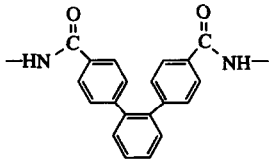
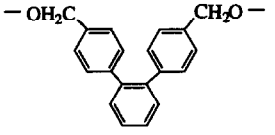
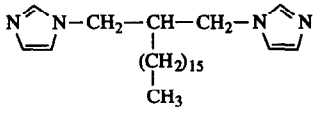


Scheme 1: Expected behaviour of suitable dimeric Mn(III)-tetrarylporphyrins in the presence of a bidentate nitrogen ligand (L-L) and H_2O_2.

Results and Discussion. Dimeric porphyrins **1a,b** and **2a,b** (Figure 1) were designed with the aim to combine the presence of an entropically favored coordination site for bidentate nitrogen bases with chemical stability under oxidative conditions. This last requirement was satisfied by selecting aromatic spacers and the robust 5,10,15,20-tetrakis-(2,6-dichlorophenyl)porphyrin as structural components of the new compounds. Most dimeric metalloporphyrins studied as receptors for bidentate bases are linked through more than one bridge in order to restrict conformational freedom. Our preference for a singly bridged model rests on the need to favor a clamshell conformation of the host molecule retaining at the same time its flexibility. This feature should facilitate the inclusion of the ligand, otherwise prevented by the high steric demand of the chlorine atoms, and provide for the solubility of the dimer. In order to modulate the conformational freedom, either amide or ether bonds were used to connect the spacer and the porphyrin rings. The catalytic activity of the Mn(III) complexes of the new compounds (Mn_2-**1a,b** and **2a,b**) was tested in cyclooctene epoxidation by 30% H_2O_2 in the presence of N,N'-bis-(2-hexadecyl-1,3-propandiyl)imidazole **3** (Figure 1), a specially devised bidentate ligand.

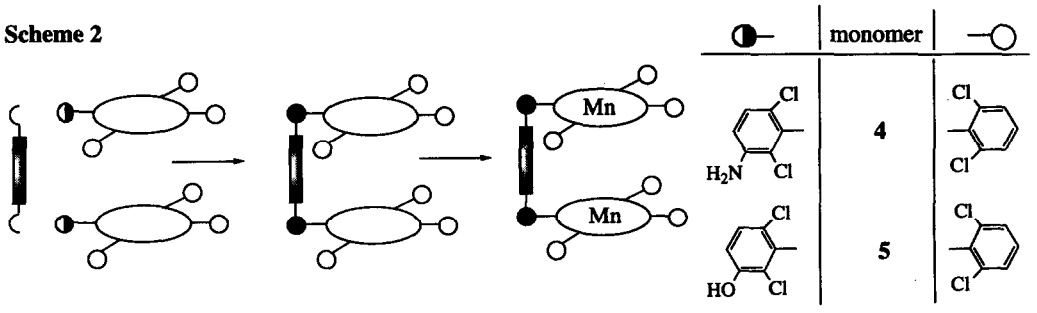
Figure 1



Compound	
1 a	
1 b	
2 a	
2 b	
3	

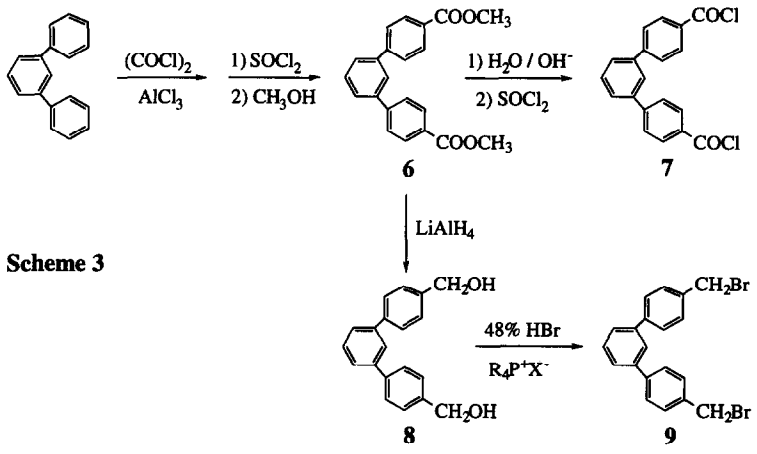
Mn_2-**1a,b** and Mn_2-**2a,b** were synthesized following the straightforward pathway outlined in Scheme 2. Two identical preformed porphyrin monomers (**4** or **5**), with a single further reactive group at the meta position of one of the *meso* aryl substituents, were allowed to react with the proper bridging agent bearing two suitable equivalent fasteners. The metal was introduced in each porphyrin unit after the assembling of the dimer.

Scheme 2



Condensation of 2,6-dichloro-3-nitrobenzaldehyde with 2,6-dichlorobenzaldehyde and pyrrole (molar ratios 1:3:4) under the general synthetic conditions described by Lindsey,[18] followed by reduction of the nitro group, afforded the starting phorpyrin **4** in 8% overall yield. The other monomer **5** was analogously prepared in 9% overall yield, starting from 2,6-dichloro-3-methoxybenzaldehyde and then deprotecting the -OCH_3 group by treatment with an excess of BBr_3.

Two of the bridging units (i.e. 1,3-dibromomethylbenzene and isophthaloylchloride) were commercially available, while **7** and **9** were synthesized starting from *m*-terphenyl (Scheme 3). The reaction of this compound with oxalyl chloride in the presence of $AlCl_3$ afforded a mixture of mono- and dicarboxylic acids insoluble in most organic solvents. The mixture was refluxed with an excess of $SOCl_2$ until complete dissolution; after distillation under vacuum, an excess of methanol was added to the solid residue. The diester **6** [19] was easily recovered by chromatography of the soluble mixture (18% yield) and finally converted into the desired diacylchloride **7** (90%) or into the dibromomethyl derivative **9** (55%).



Scheme 3

N-Acylation of **4** with the proper diacyl chloride in the correct stoichiometric ratio was carried out in dry dimethylacetamide at room temperature in the absence of any other base, affording **1a** and **2a** in 67% and 55% yield respectively. O-Alkylation of **5** with 1,3-dibromomethylbenzene or **9**, carried out in DMF with Cs_2CO_3 as base, gave **1b** and **2b** with the same yield (50%). All the dimeric tetraarylporphyrins thus synthesized were quantitatively converted into their Mn(III) complexes following reported procedures.[20]

The complete substitution of the ortho hydrogen atoms of the *meso*-aryl groups with chlorine is essential in order to achieve the required resistance of the catalysts under oxidative conditions, but it hinders the possible application of some elegant and convenient synthetic routes leading either to the unsymmetrically functionalized monomers [21] or to the dimers [1,2].

According to CPK models and MM2 molecular mechanics calculations, the preferred conformations of the new dimeric phorphyrins meet the geometric requirements for the inclusion of a certain number of bidentate heterocyclic nitrogen bases. Preliminary experiments showed that most of them (e.g. N,N'-diimidazolylmethane, 4,4'-dipyridylmethane, 4,4'-dipyridyl) were inefficient as co-catalysts in the aqueous/organic two-phase conditions under which reactions were carried out. This finding was not completely unexpected, since the hydrophilicity of such bases prevents their complete partition in the organic phase. Better results were obtained using the lipophilic bidentate ligand **3** (Figure 1) that was designed taking into account this essential factor.[22]

UV-Vis spectrophotometric titration and mass spectrometry (MS-FAB$^+$) were employed in order to determine the real structure of the complex formed by the association of Mn_2-**1** or Mn_2-**2** and **3**. The former method has

been largely exploited in the study of host-guest chemistry of dimeric Zn(II)-porphyrins, allowing the measurement of the binding constants K_D and the determination of the stoichiometry of the complexes formed with bidentate nitrogen bases.[23] Due to the more complicated coordination behaviour of Mn(III)- with respect to Zn(II)-dimeric porphyrins we did not succeed in evaluating these features satisfactorily. However, a noticeable difference exists between the behaviour observed by adding the bidentate base **3** and that observed by adding N-hexylimidazole **10** to a solution of Mn_2-**1** (or Mn_2-**2**). In the former case the Soret absorption band associated to the non-axially coordinated Mn(III)-porphyrin almost entirely disappears by addition of 1 molar equivalent of **3**, the disappearance being complete by addition of 10 equivalents. With the monodentate ligand **10** the disappearance of the Soret band is more gradual, and is almost total only after the addition of 100 molar equiv. of ligand. Comparative MS-FAB$^+$ experiments carried out on samples obtained by adding either N-butylimidazole or **3**, or both, to CH_2Cl_2 solutions of Mn_2-**1** (or Mn_2-**2**) at known concentration, showed that in the presence of **3** only an 1/1 adduct was present in the gas phase, and that it was actually an inclusion complex.[24]

Catalytic activity of the new compounds was tested in the epoxidation of cyclooctene using 30% H_2O_2 as oxygen donor. The reactions were carried out under H_2O/CH_2Cl_2 two-phase conditions at 0°C in the presence of sodium benzoate (A).[14] The pH of 30% H_2O_2 was adjusted at 4.5-5.0 with NaOH 1% and the lipophilic bidentate ligand **3** was added to the CH_2Cl_2 solution of the dimeric catalyst (P) before starting the reaction. The olefin conversion and the yield in epoxide at different times were determined by gas-chromatographic analysis of the organic phase: for each reaction carried out, selectivity in epoxide was 100%. The results obtained are summarized in Table 1.

Table 1: Cyclooctene epoxidation promoted by 30% H_2O_2 catalyzed by dimeric Mn(III)-tetraarylporphyrins [a]

Catalyst (P)	**Ligand** (L)	**Molar Ratio** Olefin/P	P/L	**Time** (min)	**Conv.**[b] %	**Turnover**[c]	**Turnover rate**[d]
Mn_2-**1a**	**3**	1000	1	60	38	380	
				120	65	650	7
Mn_2-**2a**	**3**	1000	1	60	45	450	
				120	70	700	9
Mn_2-**1b**	**3**	1000	1	60	100	1000	110
Mn_2-**2b**	**3**	1000	1	60	100	1000	125
Mn_2-**1b**	**3**	2000	1	60	75	1500	75
Mn_2-**2b**	**3**	2000	1	60	75	1500	75
Mn_2-**1b**	**10**	2000	2	60	90	1800	100
Mn_2-**2b**	**10**	2000	2	60	92	1840	100

[a] In CH_2Cl_2, pH 4.5, T = 0 °C, in the presence of sodium benzoate (A). Molar ratio A/P = 4, H_2O_2/olefin = 2. [b] Selectivity (Epoxide/converted olefin) =100%. [c] mmol epoxide/mmol P. [d] mmol epoxide/mmol P·min, values calculated at 50% conversion.

Operating with molar ratios olefin:P = 1000, H_2O_2:P = 2000, A:P = 4 and **3**:P = 1, the complete epoxidation of cyclooctene catalyzed by Mn_2-**1b** and Mn_2-**2b** required 50 and 40 min, respectively. The turnover rates calculated at 50% olefin conversion were 110 and 125 mmol product/mmol catalyst · min, respectively. Mn_2-**1a** and Mn_2-**2a** happened to be less efficient catalysts, the conversion of the substrate being not complete after 120 min. The overall turnover for the two catalysts was 700 and 800, respectively.

Another series of reactions was carried out under the same conditions in the presence of Mn_2-**1b** or Mn_2-**2b**, this time operating with molar ratio olefin:P = 2000. Both the catalysts allowed to reach 75% conversion of the substrate in 60 min, i.e. an overall number of 1500 catalytic cycles or 750 cycles for each metal site, with turnover rates calculated at 50% conversion of 75 mmol product/mmol catalyst · min. The catalytic activity of Mn_2-**1b** and Mn_2-**2b** in the presence of N-hexylimidazole **10** as axial ligand was also tested. Operating with molar ratios olefin:P = 2000 and **10**:P = 2 we obtained 90% conversion of cyclooctene in 60 min with both the catalysts, i.e. an overall number of 1800 catalytic cycles with turnover rates calculated at 50% conversion of 100 mmol product/mmol catalyst · min.

The results described above show that the new suitably designed dimeric Mn(III)-tetraarylporphyrins are effective catalysts for olefin epoxidation promoted by 30% H_2O_2. The nature of the bonds between the spacer and the porphyrin moieties is the most important factor in determining their catalytic efficiency, which is only slightly affected by the nature of the spacer. This behaviour can be related to the higher flexibility of dimeric complexes linked through ether bonds in comparison to those featuring amide bonds. The catalytic efficiency of dimeric metalloporphyrins Mn_2-**1b** or Mn_2-**2b** in the presence of **3**, condition under which the existence in solution of an inclusion complex type **B** (Scheme 1) is highly probable, approaches those of the most efficient systems based on metallo-porphyrins reported in the literature.[14] Thus this first attempt to use dimeric metalloporphyrins as catalysts for hydrocarbon oxygenations was succesful. However, contrary to our expectation, the use of the bidentate ligand **3** instead of its monodentate counterpart does not improve the efficiency of the dimeric catalysts. It is worth to remember that the selection of a bidentate ligand able to act as co-catalyst under the reported reaction conditions was not a simple matter. We cannot exclude that further studies that we have presently undertaken could lead to the synthesis of bidentate ligands more efficient than **3**, showing an opposite behaviour.

Experimental section. ^{1}H-NMR spectra were recorded on a Bruker WP80SY spectrometer in $CDCl_3$ as solvent. UV-Vis spectra were obtained with a Lambda 6 Perkin-Elmer spectrophotometer. Fast atom bombardment mass spectra of the compounds were obtained on an Analytical VG 7070 EQ instrument; FAB-MS spectrometry experiments carried out in order to elucidate the nature of the complexes were performed by Dr. F.M. Rubino on a Finnigan MAT90 instrument. Molecular mechanics calculations using the MM2 force field in MACROMODEL are due to the courtesy of Dr. L. Raimondi. Melting point were taken on a Buchi 535 apparatus and are uncorrected. GC analyses were performed on a Varian Model 3700 gas chromatograph flame ionization instrument (20 x 0.125 in. OV-101-5% on CHP 100-125 mesh column).

N,N'-bis-(2-hexadecyl-1,3-propandiyl)imidazole **3**. - A sample of 60% NaH (0.50 g, 12.5 mmol) in mineral oil was added to a stirred solution of imidazole (0.68 g, 10 mmol) in dry THF (30 ml) at RT. Stirring was maintained for 60 min, then

tetrabutylammonium bromide (0.32 g, 1 mmol) and 1,3-ditosyl-2-*n*-hexadecyl-propane (1.83 g, 3 mmol) were added. After 8 h at reflux the solvent was evaporated and the reaction mixture taken up in H_2O (30 ml) was extracted with CH_2Cl_2 (3x50 ml). Chromatography of the combined organic extracts (silica-gel, AcOEt/CH_3OH 9/1) afforded **3** (1.18 g, 30% yield).

Anal. calc. for $C_{25}H_{44}N_4$: C, 74.95; H, 11,07; N, 13.98. Found: C, 74.88; H, 11.19; N, 13.87.

^{1}H-NMR (80 MHz, $CDCl_3$): δ = 0.90 (3H, t), 1.24-1.40 (30H, m), 2.22 (1H, m), 3.80 (4H, m), 6.80-7.08 (4H, d), 7.40 (2H, s).

5-(2,6-dichloro-3-aminophenyl)-10,15,20-tri-(2,6-dichlorophenyl)porphyrin **4**.- A solution of 2,6-dichlorobenzaldehyde (1.57 g, 9 mmol), 2,6-dichloro-3-nitrobenzaldehyde (0.66 g, 3 mmol), pyrrole (0.85 g, 12 mmol) and BF_3·Et_2O (0,57 g, 4 mmol) in CH_2Cl_2 freshly distilled over P_2O_5 (1200 ml), was stirred at RT for 15 h. After addition of 2,3-dichloro-5,6-dicyano-1,4-benzoquinone (DDQ, 1.81 g, 8 mmol) the reaction mixture was stirred for a further 2 h, then Et_3N (1 ml) was added and the solvent evaporated. The residue was supported on Florisil (40 g) and purified by column chromatography (neutral alumina, eluant light petroleum/CH_2Cl_2 1/1). 5,10,15,20-tetrakis-(2,6-dichlorophenyl)porphyrin (432 mg) was the first porphyrin eluted, followed by slightly impure 5-(2,6-dichloro-3-nitrophenyl)-10,15,20-tri-(2,6-dichlorophenyl)porphyrin (290 mg). This last product was suspended in 36% HCl (70 ml), the temperature raised to 80 °C and $SnCl_2$·$2H_2O$ (3.7 g) added to the mixture. After 2 h of vigorous stirring the mixture was cooled at 0 °C, diluted with H_2O (40 ml) and then extracted with CH_2Cl_2 (3x100 ml). The combined organic extracts were washed with aqueous 15% NH_4OH (20 ml), brine (3x20 ml), and dried on Na_2SO_4. Column chromatography of the residue (silica-gel, light petroleum/CH_2Cl_2 7/3) afforded **4** (240 mg) which was dissolved in CH_2Cl_2 (10 ml) and reprecipitated by adding *n*-pentane. This procedure afforded pure **4** (215 mg, 8% yield with respect to pyrrole).

^{1}H-NMR (300 MHz, $CDCl_3$): δ = -2.55 (2H, br s), 4.30-4.40 (2H, br s), 7.54-7.80 (11H, m), 8.75 (8H, s).

MS-FAB$^+$: m/z 900 (lowest mass peak of isotope cluster); $C_{44}H_{23}Cl_8N_5$ requires M = 905.

UV-Vis (CH_2Cl_2): λ_{max} (log ε) = 418.5 nm (5.53).

5-(2,6-dichloro-3-hydroxyphenyl)-10,15,20-tri-(2,6-dichlorophenyl)porphyrin **5**.- A solution of 2,6-dichlorobenzaldehyde (1.57 g, 9 mmol), 2,6-dichloro-3-methoxybenzaldehyde (0.62 g, 3 mmol), pyrrole (0.85 g, 12 mmol) and BF_3·Et_2O (0,57 g, 4 mmol) in CH_2Cl_2 freshly distilled over P_2O_5 (1200 ml), was stirred at RT for 8 h. After addition of tetrachloro-1,2-benzoquinone (*o*-chloranil, 1.84 g, 7.5 mmol) the reaction mixture was stirred for a further 1 h then the solvent evaporated. The residue was supported on Florisil (40 g) and purified a first time by column chromatography (neutral alumina, light petroleum/CH_2Cl_2 1/1) thus separating 5,10,15,20-tetrakis-(2,6-dichlorophenyl)porphyrin (240 mg) from 5-(2,6-dichloro-3-methoxyphenyl)-10,15,20-tri-(2,6-dichlorophenyl)porphyrin (340 mg). This last product was further purified by column chromatography (silica-gel, light petroleum/CH_2Cl_2 1/1) and dissolved in dry CH_2Cl_2 (50 ml). After cooling at 0 °C, BBr_3 (4 ml, solution 1M in CH_2Cl_2) was added under Ar to the stirred solution. The reaction temperature was allowed to warm up to RT and after 24 h the mixture was poured into 150 g of crushed ice and vigorously stirred for 30 min. The organic phase was separated and the aqueous layer was extracted with CH_2Cl_2 (2x100 ml); the combined organic layers were washed with aqueous 5% $NaHCO_3$ (30 ml), brine (3x20 ml) and dried on Na_2SO_4. After evaporation of the solvent, column chromatography (silica-gel, light petroleum/CH_2Cl_2 7/3 then CH_2Cl_2 and finally CH_2Cl_2/CH_3OH 95/5) afforded pure **5** (250 mg, 9% yield with respect to pyrrole).

^{1}H-NMR (300 MHz, $CDCl_3$): δ = -2.50 (2H, br s), 5.85 (1H, s), 7.45-7.83 (12H, m), 8.67 (8H, s).

MS-FAB$^+$: m/z cluster 906 (100%); $C_{44}H_{22}Cl_8N_4O$ requires M = 906.

UV-Vis (CH_2Cl_2): λ_{max} (log ε) = 418 nm (5.49).

4,4"-dicarbomethoxy-1,1':3',1"-terphenyl **6**.- Oxalyl chloride (6.09 g, 48 mmol) was added over 10 min to a stirred suspension of $AlCl_3$ (6.38 g, 48 mmol) in CS_2 (40 ml) cooled at -5 °C. After further 15 min a solution of *m*-terphenyl (4.61 g, 20 mmol) in CS_2 (60 ml) was added dropwise to the mixture keeping the temperature below 5 °C. After the addition, stirring went on at the same temperatutre for 30 min, then at reflux for 3 h. The mixture was cooled and poured slowly into stirred crushed ice (150 g) containing HCl (360 mmol). The organic phase was separated and the aqueous layer was extracted with CH_2Cl_2 (3x75 ml); the combined organic extracts were washed with brine (3x30 ml) obtaining a slightly turbid solution. Drying on $MgSO_4$ and evaporation of the solvent afforded a yellow solid (5.43 g). It was treated with $SOCl_2$ (20 ml) and the mixture was refluxed until it was completely dissolved (2 h). The excess of $SOCl_2$ was eliminated by distillation under vacuum and the solid residue was refluxed for 3 h with CH_3OH (50 ml). Column chromatography (silica-gel, CH_2Cl_2/light petroleum 7/3) of the solid obtained after evaporation of the alcohol gave crude **6** (1.75 g, m.p. = 182-186 °C). Recrystallization from glacial CH_3COOH afforded pure **6** (1.25 g, 18% yield, m.p. = 192 °C).

Anal. calc. for $C_{22}H_{18}O_4$: C, 76.29; H, 5.24. Found: C, 76.23; H, 5.30.

^{1}H-NMR (80 MHz, $CDCl_3$): δ = 3.90 (6H, s), 7.53-7.80 (8H, m), 8.02-8.25 (4H, m).

4,4"-Bis(hydroxymethyl)-1,1':3',1"-terphenyl **8**.- A solution of **6** (1.04 g, 3 mmol) in dry THF (15 ml) was added dropwise to a stirred suspension of $LiAlH_4$ (0.16 g, 4 mmol) in dry THF (25 ml) at a rate sufficient to allow the solvent to reflux. At the end of the addition stirring went on for further 3 h under reflux, then the mixture was cooled and cautiously acidified with 5% H_2SO_4. The organic phase was separated and the aqueous layer was extracted with CH_2Cl_2 (2x15 ml); the combined organic phase were evaporated, the residue taken up into CH_2Cl_2 (50 ml) and washed with brine (2x20 ml). Drying on $MgSO_4$ and evaporation of the solvent afforded **8** (560 mg, 64% yield, m.p.= 191-192 °C) pure enough for the further reaction.

Anal. calc. for $C_{20}H_{18}O_2$: C, 82.73; H, 6.25. Found: C, 82.60; H, 6.15.

^{1}H-NMR (80 MHz, $CDCl_3$): δ = 1.40-1.60 (2H, br s), 4.72 (4H, s), 7.35-7.80 (12H, m).

4,4"-Bis(bromomethyl)-1,1':3',1"-terphenyl **9**.- A mixture of 48% HBr (1.12 ml, 20 mmol), hexadecyltributylphosphonium bromide (51 mg, 0.1 mmol) and **8** (290 mg, 1 mmol) was stirred at 105 °C for 12 h. After cooling, H_2O (10 ml) and CH_2Cl_2 (15 ml) were added. The organic phase was separated, washed with H_2O (10 ml), aqueous 5% $NaHCO_3$ (10 ml), H_2O (10 ml) and dried on $MgSO_4$. After evaporation of the solvent, column chromatography (silica-gel, light petroleum/Et_2O 1/1) afforded **9** (360 mg, 86% yield, m.p.= 122 °C).

Anal. calc. for $C_{20}H_{16}Br_2$: C, 57.72; H, 3.88; Br, 38.40. Found: C, 57.68; H, 3.79; Br, 38.51.

^{1}H-NMR (80 MHz, $CDCl_3$): δ = 4.60 (4H, s), 7.40-7.82 (12H, m).

Bis-{5,5'-[3-(1,3-dicarbamoylbenzen)-2,6-dichlorophenyl]-10,10',15,15',20,20'-tri-(2,6-dichlorophenyl)}-porphyrin **1a**. - A solution of porphyrin **4** (74 mg, 0.082 mmol) and isophthaloylchloride (8 mg, 0.041 mmol) in dry dimethylacetamide (15 ml) was stirred at RT for 48 h. Evaporation of the solvent and column chromatography (silica-gel, CH_2Cl_2) gave **1a** (65 mg) which was dissolved in CH_2Cl_2 (10 ml) and reprecipitated by adding *n*-pentane. This procedure afforded pure **1a** (53 mg, 67% yield).

^{1}H-NMR (80 MHz, $CDCl_3$): δ = -2.50 (4H, br s), 3.25-3.80 (2H, br s), 7.60-7.90 (22H, m), 8.05-8.15 (4H, m), 8.60-8.80 (12H, m), 9;20 (4H, d).

MS-FAB$^+$: m/z cluster 1941 (100%); $C_{96}H_{48}Cl_{16}N_{10}O_2$ requires M = 1941

UV-Vis (CH_2Cl_2): λ_{max} (log ε) = 417 nm (5.85).

Bis-{5,5'-[3-(1,3-dicarbamoylbenzen)-2,6-dichlorophenyl]-10,10',15,15',20,20'-tri-(2,6-dichlorophenyl)}-porphyrin Mn(III) chloride complex Mn_2-**1a**. - A solution of **1a** (58 mg, 0.03 mmol) in DMF (30 ml) was stirred under reflux with $Mn(OAc)_2 \cdot 4H_2O$ (735 mg, 3 mmol) for 8 h. After evaporation of the solvent *in vacuo*, the residue was dissolved in CH_2Cl_2 (150 ml) and washed with water (2x30 ml). TLC (silica-gel, CH_2Cl_2/MeOH 95:5) showed the complete disappearence of the starting material and UV-Vis spectroscopy the absence of non metallated porphyrin rings. Column chromatography (silica-gel, CH_2Cl_2/MeOH 9:1) afforded a dark brown powder (65 mg) that was dissolved in CH_2Cl_2 (50 ml) and stirred with a saturated NaCl aqueous solution (50 ml). The organic phase was dried over $MgSO_4$ and the solvent evaporated, affording pure Mn_2-**1a** (56 mg, 90% yield).

MS-FAB$^+$: m/z cluster 2047 (100%); $(C_{96}H_{44}Cl_{16}N_{10}O_2)Mn_2$ requires M = 2047

UV-Vis (CH_2Cl_2): λ_{max} (log ε) = 477.4 nm (5.40).

Bis-{5,5'-[3-(1,3-dimethylenoxybenzen)-2,6-dichlorophenyl]-10,10',15,15',20,20'-tri-(2,6-dichloro-phenyl)}porphyrin **1b**. - A suspension of porphyrin **5** (82 mg, 0.09 mmol), 1,3-dibromomethylbenzene (302 mg, 0.18 mmol) and solid Cs_2CO_3 (162 mg, 0.5 mmol) in dry DMF (15 ml) was stirred overnight at RT. Evaporation of the solvent and column chromatography (silica-gel, light petroleum/CH_2Cl_2 1/1) afforded **1b** (43 mg, 50% yield).

^{1}H-NMR (80 MHz, $CDCl_3$): δ = -2.55 (4H, br s), 5.35 (4H, s), 7.38-7.80 (24H, m), 8.60-8.75 (16H, m).

MS-FAB$^+$: m/z cluster 1914 (100%); $C_{96}H_{50}Cl_{16}N_8O_2$ requires M = 1914

UV-Vis (CH_2Cl_2): λ_{max} (log ε) = 418 nm (5.87).

Bis-{5,5'-[3-(1,3-dimethylenoxybenzen)-2,6-dichlorophenyl]-10,10',15,15',20,20'-tri-(2,6-dichloro-phenyl)}porphyrin Mn(III) chloride complex Mn_2-**1b**.- The title compound was obtained in 85% yield as reported for Mn_2-**1a**.

MS-FAB$^+$: m/z cluster 2020 (100%); $(C_{96}H_{46}Cl_{16}N_8O_2)Mn_2$ requires M = 2020.

UV-Vis (CH_2Cl_2): λ_{max} (log ε) = 478 nm (5.45).

Bis-{5,5'-[3-[4,4'-dicarbamoyl-1,1':3':1"terphenyl)-2,6-dichlorophenyl]-10,10',15,15',20,20'-tri-(2,6-dichlorophenyl)}porphyrin **2a**. - The title compound was obtained in 57% yield from **4** and diacyl chloride **7** as reported for **1a**.

^{1}H-NMR (80 MHz, $CDCl_3$): δ = -2.60 (4H, br s), 7.90-8.32 (34H, m), 8.58-8.92 (16H, m), 11.10 (2H, s).

MS-FAB$^+$: m/z cluster 2092 (100%); $C_{108}H_{56}Cl_{16}N_{10}O_2$ requires M = 2092.

UV-Vis (CH_2Cl_2): λ_{max} (log ε) = 418 nm (5.79).

Bis-{5,5'-[3-[4,4'-dicarbamoyl-1,1':3':1"terphenyl)-2,6-dichlorophenyl]-10,10',15,15',20,20'-tri-(2,6-dichlorophenyl)}porphyrin Mn(III) chloride complex Mn_2-**2a**.- The title compound was obtained in 87% yield as reported for Mn_2-**1a**.

MS-FAB$^+$: m/z cluster 2199 (100%); $(C_{108}H_{52}Cl_{16}N_{10}O_2)Mn_2$ requires M = 2199.

UV-Vis (CH_2Cl_2): λ_{max} (log ε) = 478 nm (5.42).

Bis-{5,5'-[3-(4,4"-dimethylenoxy-1,1':3',1"-terphenyl)-2,6-dichlorophenyl]-10,10',15,15',20,20'-tri-(2,6-dichloro-phenyl)}porphyrin **2b**. - The title compound was obtained in 50% yield from **5** and **9** as reported for **1b**.

^{1}H-NMR (80 MHz, $CDCl_3$): δ = -2.55 (4H, br s), 5.45 (4H, s), 7.38-7.80 (84H, m), 8.60-8.70 (16H, m).

MS-FAB$^+$: m/z cluster 2068 (100%); $C_{108}H_{58}Cl_{16}N_8O_2$ requires M = 2068.
UV-Vis (CH_2Cl_2): λ_{max} (log ε) = 417 nm (5.80).

Bis-{5,5'-[3-(4,4"-dimethylenoxy-1,1':3',1"-terphenyl)-2,6-dichlorophenyl]-10,10',15,15',20,20'-tri-(2,6-dichloro-phenyl)}porphyrin Mn(III) chloride complex Mn_2-**2b**.- The title compound was obtained in 80% yield as reported for Mn_2-**1a**.
MS-FAB$^+$: m/z cluster 2172 (100%); $(C_{108}H_{54}Cl_{16}N_8O_2)Mn_2$ requires M = 2172.
UV-Vis (CH_2Cl_2): λ_{max} (log ε) = 478.3 nm (5.38).

UV-Vis spectrophotometric titration. Samples (5ml) of a 1.0 x 10^{-5} M solution of P in CH_2Cl_2 were placed in 10 ml volumetric flasks (class A) by means of a Metrohm 655 Dosimat. To each of these flasks was then added a CH_2Cl_2 solution of ligand **3** or **10** (0.1+5 ml, concentration 1.0 x 10^{-4} M +1.0 x 10^{-2} M): both the volume and concentration of the ligand solution were chosen according to the desired L/P molar ratio (0.1+200). The volume of each flask was brought to 10 ml and the shift in Soret absorption on ligation was followed. Increasing the ratio L/P the Soret peak intensity decreased and the maximal absoption shifted to lower wavelengths, but the new maxima were spread out and we could not observe a well-defined isosbestic point. It also turned out impossible to calculate exactly the value of the binding constants using a procedure we previously followed for monomeric Mn(III)-porphyrins.[14]

Cyclooctene Epoxidation. Reactions were carried out in a 20 ml flask equipped with a teflon lined screw cap and magnetic stirrer, thermostatted at 0 ± 0.2°C with circulating ethanol by a Haake F3 Cryostat. Stirring was maintained at the maximal rate achievable (1300 ± 50 rpm) in order to ensure the best contact between the organic and the aqueous phase.
For reactions carried out with molar ratio olefin/P = 1000 (Table 1), the flask was charged with: (i) 1 ml of a 2.50 x 10^{-3} M solution of dimeric Mn(III)-porphyrin (P) in CH_2Cl_2; (ii) 1 ml of a 2.50 M solution of cyclooctene in CH_2Cl_2 containing decane (1.25 M) as internal standard for gas-chromatograpy; (iii) 10 µl of a 2.50 x 10^{-1} M solution of **3** in CH_2Cl_2. For reactions carried out with molar ratio olefin/P = 2000 (Table 1), the flask was charged with: 1 ml of a 1.25 x 10^{-3} M solution of P in CH_2Cl_2; (ii) 1 ml of a 2.50 M solution of cyclooctene in CH_2Cl_2 containing decane (1.25 M); (iii) 10 µl of a 1.25 x 10^{-1} M solution of **3** in CH_2Cl_2. The solution was stirred 5 min then 0.5 ml of 30% H_2O_2 (~10 M, 2 molar equivalents with respect to the substrate) were added to the flask. The pH of 30% H_2O_2 was previously adjusted to 4.5-5.0 with 1% NaOH and an amount of sodium benzoate (A) satisfying the required molar ratio P/A = 4 (these solutions were generally prepared on a 5 ml scale, stored at 0°C, and used within one hour from their preparation). The mixture was stirred and samples were taken at different times and analysed by G.C.

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References and notes.

(1) D. Dolphin, J. Hiom, J. P. Paine III; *Heterocycles*, **1981**, *16*, 417.

(2) See the references cited in B. C. Bookser, T. C. Bruice; *J. Am. Chem. Soc.*, **1991**, *113*, 4208.

(3) (a) D. Gust, T. A. Moore; *Science*, **1989**, *244*, 35. (b) K. Maruyama, A. Osuka; *Pure Appl. Chem.*, **1990**, *62*, 1511. (c) J.-C. Chambron, A. Harriman, V. Heitz, J.-P. Sauvage; *J. Am. Chem. Soc.*, **1993**, *115*, 7419.

(4) (a) J. P. Collman, P. Denisevich, Y. Konai, C. Koval, F. C. Anson; *J. Am. Chem. Soc.*, **1980**, *102*, 6027. (b) H. Y. Liu, M. J. Weaver, C. B. Wang, C. K. Chang; *J. Electroanal. Chem. Interfacial Electrochem.*, **1983**, *145*, 439.

(5) J. P. Collman, Y. Ha, P. S. Wagenknecht, M.-A. Lopez, R. Guilard; *J. Am. Chem. Soc.*, **1993**, *115*, 9080.

(6) I. Tabushi; *Pure Appl. Chem.*, **1988**, *60*, 581.

(7) A. Hamilton, J.-M. Lehn, J. L. Sessler; *J. Am. Chem. Soc.*, **1986**, *108*, 5158.

(8) S. Anderson, H. L. Anderson, J. K. M. Sanders; *Acc. Chem. Res.*, **1993**, *26*, 469.

(9) B. Meunier; *Chem. Rev.*, **1992**, *92*, 1411.

(10) (a) F. Montanari, M. Penso, S. Quici, P. Vigano; *J. Org.Chem.*, **1985**, *50*, 4888. (b) S. Banfi, F. Montanari, S. Quici; *Recl. Trav. Chim. Pays-Bas*, **1990**, *109*, 117.

(11) F. Montanari, S. Banfi, S. Quici, G. Pozzi; *Rev. Heteroatom Chem.*, **1992**, *6*, 94.

(12) The effective nature of this species strongly depends on the reaction conditions. In the presence of nitrogen axial ligands a transiently stable Mn(V)-oxo porphyrin species is believed to be the oxidizing intermediate. (a) J. T. Groves, M. K. Stern; *J. Am. Chem. Soc.*, **1988**, *110*, 8628. (b) D. Ostovic, T. C. Bruice; *Acc. Chem. Res.*, **1992**, *25*, 314. (c) R. D. Arasasingham, G.-X He, T. C. Bruice; *J. Am. Chem. Soc.*, **1993**, *115*, 7985.

(13) (a) P. Battioni, J.-P. Renaud, J.-F. Bartoli, D. Mansuy; *J. Chem. Soc., Chem. Commun.*, **1986**, 341. (b) P. Battioni, J.-P. Renaud, J.-F. Bartoli, M. Reina-Artiles, M. Fort, D. Mansuy; *J. Am. Chem. Soc.*, **1988**, *110*, 8462.

(14) P. L. Anelli, S. Banfi, F. Legramandi, F. Montanari, G. Pozzi, S. Quici; *J. Chem. Soc., Perkin Trans.I*, **1993**, 1345 and reference therein.

(15) Y. Naruta, K. Maruyama; *J. Am. Chem. Soc.*, **1991**, *113*, 3595.

(16) J. T. Landrum, C. A. Reed, K. Hatano, W. Robert Scheidt; *J. Am. Chem. Soc.*, **1978**, *100*, 3232.

(17) I. Tabushi, S. Kugimiya, M. G. Kinnaird, T. Sasaki; *J. Am. Chem. Soc.*, **1985**, *107* ,4192.

(18) (a) J. S. Lindsey, I. C. Schreiman, H. C. Hsu, P. C. Kearney, A. M. Marguerettaz; *J. Org. Chem.*, **1987**, *52*, 827. (b) J. S. Lindsey, R. W. Wagner; *J. Org. Chem.*, 1989, **54**, 828.

(19) G. Rabilloud, B. Masson, B. Sillion, N. Platzer, J.-J. Basselier; *Bull. Soc. Chim. France*, **1977**, 281. In this paper a different synthetic procedure leading to **6** (8% yield) is described.

(20) A. D. Adler, F. R. Longo, F. Kampes, J. Kim; *J. Inorg. Nucl. Chem.*, **1970**, *32*, 2443.

(21) D. M. Wallace, K. M. Smith; *Tetrahedron Lett.*, **1990**, *31*, 7265.

(22) For a general discussion on the importance of the lipophilicity of the axial ligand see ref. 11.

(23) (a) C. A. Hunter, M. N. Meah, J. K. M. Sanders; *J. Am. Chem. Soc.*, **1990**, *112*, 5773. (b) H. L. Anderson, C. A. Hunter, M. N. Meah, J. K. M. Sanders; *J. Am. Chem. Soc.*, **1990**, *112*, 5780. (c) S. Kugimiya; *J. Chem. Soc., Chem. Commun.*, **1990**, 432. (d) I. P. Danks, I. O. Sutherland, C. H. Yap; *J. Chem. Soc., Perkin Trans. I*, **1990**, 421.

(24) We recently showed that Fast Atom Bombardment mass spectrometry (MS-FAB) is a suitable technique for the structural analysis of supramolecular Mn(III)-tetraarylporphyrin species: (a) F. M. Rubino, S. Banfi, G. Pozzi, S. Quici; *J. Am. Soc. Mass Spectrom.*, **1993**, *4*, 248. (b) F. M. Rubino, S. Banfi, G. Pozzi, S. Quici; *J. Am. Soc. Mass Spectrom.*, **1993**, *4*, 255. Preliminary results of the competitive experiments : S. Banfi, F. Montanari, G. Pozzi, S. Quici, F. M. Rubino; *Rend. Acc. Lincei, Rome*, in press. Further details will be published elsewhere.

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