Asymmetric Epoxidation of 1,2-Dihydronaphthalene Catalyzed by Manganese Chiroporphyrins: Stereoinduction Directed by Steric Exclusion

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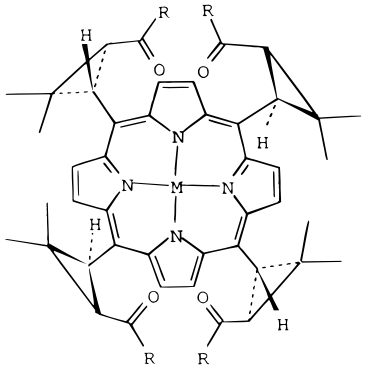
Asymmetric induction in metal-catalyzed olefin oxidations is usually explained by a combination of steric and electronic interactions between substrate and catalyst in the transition state.[1−3] Various chiral oxo transfer catalysts based on Mn(salen)[4−6] and Mn− or Fe−porphyrin complexes[7−10] have been designed in such a way that steric interaction between the substituted olefin and the dissymmetric ligand is maximized in a side-on approach transition state,[11] but electronic factors have been shown to influence also the enantioselectivity. We have prepared an extensive series of D_2-symmetric chiroporphyrins[12−16] **1a**−**l** (M = 2H) derived from enantiopure biocartol esters[17,18] and amides,[19] in which potentially stereogenic groups sit on the porphyrin ring in the vicinity of the metal-binding site, and we have screened their manganese complexes **2a**−**l** (M = MnCl) as possible asymmetric epoxidation catalysts. We have also solved the crystal structures of the nickel derivatives **3a**,**b**,**d**−**g**,**i**,**k** (M = Ni). We report that high levels of stereoinduction can be obtained with the most sterically crowded catalysts, and that the enantioselectivity of 1,2-dihydronaphthalene epoxidation is correlated to the degree of nonplanar distortion of the porphyrin.



a : R = OMe
b : R = OEt
c : R = OBn
d : R = ONp
e : R = OPh-*p*-NO_2
f : R = OPh-*m*-NO_2
g : R = O(1*S*)-*endo*-bornyl
h : R = OBu^t
i : R = N(Me)Ph
j : R = N(Et)Ph
k : R = N(Cy)C(O)NH(Cy)
l : R = NH(Cy)
Cy = cyclohexyl

Condensation of pyrrole with the appropriately substituted biocartol ester or amide followed by aromatization with DDQ afforded the chiroporphyrins **1a**−**l** atroposelectively as the desired $\alpha\beta\alpha\beta$ atropisomers. The X-ray structure[20] of the Ni complex **3g** derived from the (1*S*)-*endo*-bornyl ester (Figure 1) illustrates its conformational flexibility. Among the four ester groups in the stable *Z* conformation,[21] two have their carbonyl oxygen atom O(3) nearly eclipsed with the α pyrrole carbon atom C(7) and the bornyl groups pointing *outward* on the upper face, while the lower face shows the opposite orientation with *inward* bornyl groups. The high symmetry of the ^{1}H NMR spectrum of **3g** in $CDCl_3$ is consistent with fast interconversion in solution, and the two conformers may lead to different levels of stereoinduction in the asymmetric epoxidation of conformationally rigid olefins.[22,23] A similar conformational equilibrium is expected in the amide derivatives **3i**−**l**. The crystal structure[20] of the ruffled Ni complex **3i** (Figure 1 and graphical abstract) shows all four amide groups in the *E* conformation with the bulkier phenyl substituents *outward*. However, rotation around the C(15)−C(16) single bond is possible in solution at room temperature,[21] and conformations of **2i**−**l** in which the vicinity of the metal center is more sterically crowded than in **2a**−**h** may be accessible in the epoxidation transition state.

The chloromanganese complexes **2a**−**l** were investigated as catalysts in the asymmetric epoxidation of 1,2-dihydronaphthalene

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(20) Crystal data for **3g**·$2C_8H_{18}$: red crystal, orthorhombic, space group $C222_1$, a = 11.9940(2) Å, b = 35.0895(8) Å, c = 22.2423(4) Å, V = 9361.0(3) Å^3 at 193 K, Z = 4; final R indices [$I > 2\sigma(I)$], R = 0.0790, R_w = 0.1840, GOF = 1.130. Crystal data for **3i**·$6HCON(CH_3)_2$: red crystal, orthorhombic, space group $P2_12_12$, a = 16.1891(8) Å, b = 21.6791(11) Å, c = 11.9781(6) Å, V = 4203.9(4) Å^3 at 193 K, Z = 2; final R indices [$I > 2\sigma(I)$], R = 0.0558, R_w = 0.1417, GOF = 1.112.
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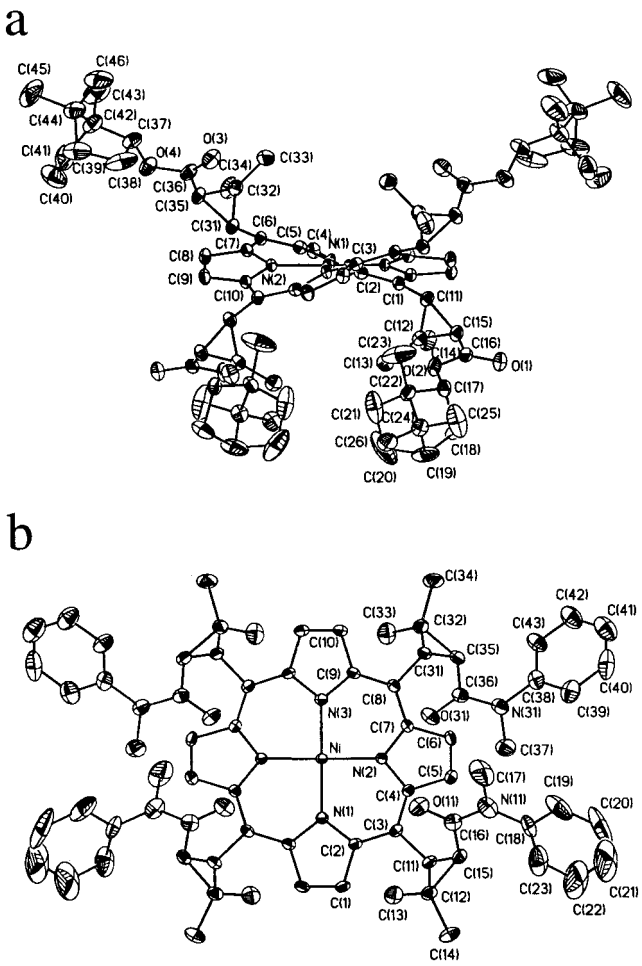

Figure 1. ORTEP views (30% probability) of the X-ray structures of nickel(II) chiroporphyrins **3g** (top) and **3i** (bottom) showing the bornyl groups pointing *outward* on the upper face and *inward* on the lower face of **3g** and the *E* conformation of the *N*-methyl, *N*-phenyl amide groups of **3i**.

4 by iodosylbenzene, and the results are collected in Table 1 (Supporting Information). The observed excess of the 1*S*,2*R* epoxide of **4** is consistent with the *Re* face selectivity expected on steric grounds for the side-on approach of the substrate (Scheme, Supporting Information). Among the eight ester derivatives, those with the bulkier substituents induce the larger enantioselectivities, and the disubstituted amides which are even bulkier bring the stereoinduction to the highest levels (86% *ee* for **4** with **2j**). This trend is illustrated by the empirical structure−enantioselectivity correlation presented in Figure 2, in which the enantiomer ratio *er* of the major 1*S*,2*R* epoxide obtained in the asymmetric epoxidation of **4** catalyzed by **2a**−**l** is plotted as a function of the NMR chemical shift of the central NH protons of **1a**−**l** *in CDCl*$_3$ *solution* (Table 1, Supporting Information). The observed correlation indicates that the enantioselectivity induced by the manganese complex increases as the aromatic character of the corresponding porphyrin free base decreases, i.e., as its degree of ruffling increases. It is important to note that the degree of porphyrin ruffling observed *in the crystal structures* of the nickel derivatives **3a**,**b**,**d**−**g**,**i**,**k** correlates poorly with the *er* of the dihydronaphthalene epoxide product, suggesting that the effect of the small size of Ni(II) and/or packing forces contribute to the observed solid-state conformations.[24] Since the degree of ruffling *in solution* reflects the steric crowding of the porphyrin,[25] it is likely that the molecular volume of the potentially stereogenic groups is the actual origin of the observed stereoinduction.[26] It is thus apparent that in these catalytic systems stereoinduction is governed by steric exclusion of the phenyl substituent of the 1,2-dihydronaphthalene substrate, a result which is consistent with a concerted oxygen atom transfer mechanism in a side-on approach transition state. We note, however, that the *ee*'s for other olefin substrates such as indene (31−52%) and 2-vinylnaphthalene (15−30%) are only low to moderate and do not reflect a single stereodirecting mechanism. Efforts are currently in progress toward a better understanding of the determinants of enantioselectivity, and particularly of the effect of porphyrin ruffling using UV−visible absorption spectroscopy, resonance Raman spectroscopy, and molecular mechanics calculations.[27]

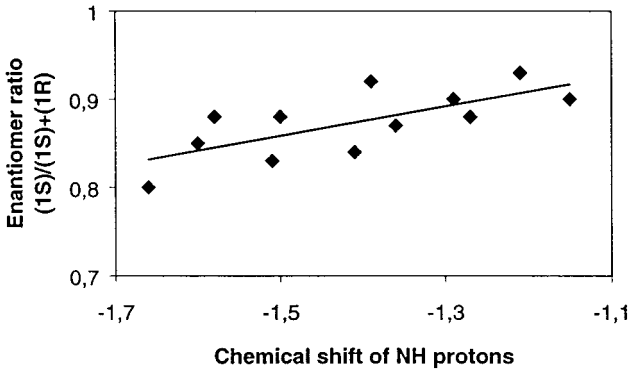

Figure 2. Plot of the enantiomer ratio *er* of the 1*S*,2*R* epoxide obtained in the asymmetric epoxidation of 1,2-dihydronaphthalene by catalysts **2a**−**l** as a function of the NMR chemical shift (ppm) of the central NH protons of chiroporphyrins **1a**−**l** in $CDCl_3$: δ −1.66 (**1a**); −1.60 (**1b**); −1.58 (**1h**); −1.51 (**1c**); −1.50 (**1f**); −1.41 (**1e**); −1.39 (**1k**); −1.36 (**1d**); −1.29 (**1i**); −1.27 (**1g**); −1.21 (**1j**); −1.15 (**1l**).

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Supporting Information Available: Scheme explaining the *Re* face selectivity; Table 1, a listing of NMR chemical shifts of the central protons of the chiroporphyrin free bases **1a**−**l** in $CDCl_3$, and of enantiomeric excesses for the epoxidation of 1,2-dihydronaphthalene with the corresponding manganese chiroporphyrin catalysts **2a**−**l**; and X-ray structural data on **3g** and **3i**. An X-ray crystallographic file, in CIF format. This material is available free of charge via the Internet at http://pubs.acs.org.

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(26) The crystal structures of **2a** and **3a** show comparable conformation and degree of ruffling of the tetramethylchiroporphyrin macrocycle in the chloromanganese(III) and nickel(II) complexes. We assume that the solution conformations of the putative oxomanganese(V) active species and parent free base are similar.
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