106. Synthetic Models of the Active Site of Cytochrome P-450

1st Communication

The Synthesis of a Doubly-Bridged Iron(II)-Porphyrin Carrying a Tightly Bound Thiolate Ligand[1])

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The doubly-bridged iron(II)-tetraphenylporphyrin derivative **6**, carrying a sterically fixed S^- ligand in the 'proximal'position and the substrate at the 'distal' site, was synthesised as an enzyme model for cytochrome P-450. Compound **36**, the CO complex of **6**, displays a split *Soret* band (403 and 457 nm) similar to the native cytochrome P-450.

Introduction. – The significance of cytochrome-P-450-catalysed oxygenations in the metabolism of endogenous compounds and xenobiotics [1] [2] has stimulated intensive research focussing on *1*) the investigation of the reaction mechanisms of P-450 monooxygenases from bacterial [3], plant [4], and mammalian [5] [6] sources, and *2*) the synthesis and application of iron-tetraphenylporphyrin derivatives, structurally related to the active site of these enzymes [7–9]. The results of these investigations led to the formulation of the catalytic cycle depicted in *Scheme 1*, in which the Fe(IV)-porphyrin radical cation **1** is believed to play a central role as the O-transfer reagent. Such species can be generated in model systems by homolytic O–O cleavage of an (acylperoxy)Fe(III)-porphyrin complex, as recently shown by *Groves* and *Watanabe* [10]. Further evidence stems from the fact, that enzyme-like substrate oxidation is observed in the reaction of **2** ('resting state') or related Fe(III)-tetraphenylporphyrin derivatives with iodosobenzene **3** [7–9], ROOH [11], and $NaIO_4$ [12]: see 'shunt-pathway', *Scheme 1*.

The unique ability of cytochrome P-450 to generate **1** *via* the O_2-binding Fe(II)-porphyrin **4** and to oxidise substrates at rather unactivated positions [3] [4] [6] [13] [14] has been attributed to the presence of a 'proximal' thiolate ligand strongly coordinating with the Fe-atom. The existence of this ligand was suggested on the basis of spectroscopical evidence [15] and experiments with model compounds [16] [17]. These indications have been verified recently by X-ray studies of $P\text{-}450_{cam.}$ [18] and the enzyme-substrate complex of $P\text{-}450_{cam.}$ [19], which identified Cys-357 as the thiolate-supplying amino acid.

Three research groups have been concerned with the syntheses of Fe(II)-porphyrins closely related to the enzymes active site (see **4**, *Scheme 1*). One of these complexes carries

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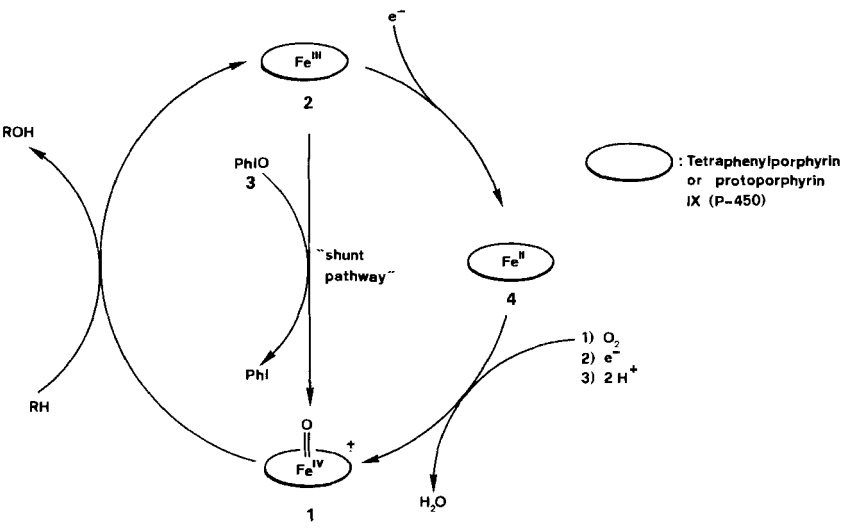
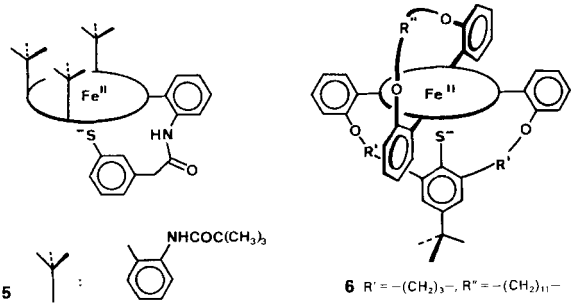
Scheme 1



a 'S⁻-bridge' [20], the others contain 'S⁻-tails' of various chain-length and structure, *e.g.* **5** [21] [22]. It was shown that these compounds form CO complexes, displaying the characteristic split *Soret* band (380 and 450 nm; calculated 325 and 430 nm [23]) of the native cytochrome P-450. However, due to the flexibility of the S⁻ attachment and subsequent equilibrium between turn-off and turn-on complexes, no O_2-binding experiments were reported and are presumably impossible to perform, since, in the presence of O_2, dimerisation *via* disulfide linkages is expected to inactivate these enzyme models.



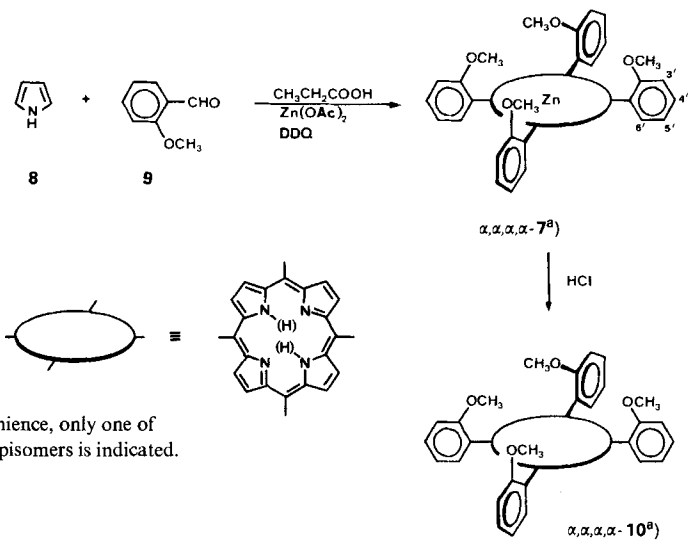
Despite all these efforts, it is still an open question how the proximal S⁻ ligand is supporting O_2 cleavage, stabilising the iron-oxen species **1**, and triggering O-transfer to the substrate. Consequently, the ultimate goal is to generate a species like **1** from the reaction of O_2 with a synthetic model carrying an S⁻ ligand in order to mimic the catalytic cycle.

To study these problems, the particularly designed enzyme model **6** was envisaged. This Fe(II)-porphyrin carries an S⁻ ligand, which for steric reasons could neither turn off

from the ligand site nor could be replaced by any other ligand present in solution. The attachment of the S^- at one bridge of the doubly-bridged tetraphenylporphyrin was considered to be the most useful, since doubly-bridged Fe-porphyrins are known to be considerably resistent against μ-oxo dimer formation in the presence of O_2 [24]. The bridge opposite to the 'S^- bridge' should be of adequate chain length and distance to the tetraphenylporphyrin plane in order to act simultaneously as the substrate. This design would allow a controlled oxidation in the presence of O_2, and in a more general sense represents a model of an enzyme-substrate complex with the covalently bound substrate.

Results and Discussion. – The most delicate problem in the synthesis of the P-450 model **6** is the attachment of the two different bridges diagonally stretching over the top ('distal') and the bottom face ('proximal') of the porphyrin. Two elegant synthetic approaches towards mixed-bridged porphyrins have been appeared before [25] and in the course [26] of our present study. *Battersby* and *Hamilton* have reported the synthesis of porphyrins with pyrrol-linked mixed bridges [25], and *Momenteau et al.* achieved the synthesis of the so called 'basket handle' porphyrins, the latter being *meso*-tetraphenylporphyrin derivatives [26].

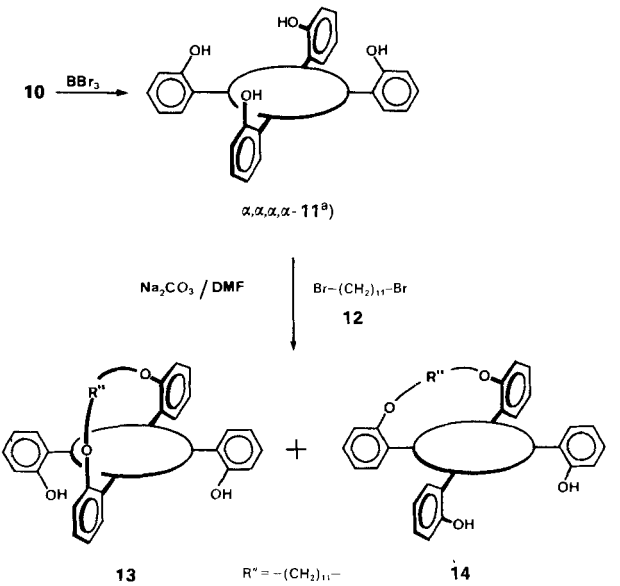
Scheme 2



a) For convenience, only one of the four atropisomers is indicated.

Our approach was similar to the latter and involved the preparation of [tetrakis(*o*-methoxyphenyl)porphyrinato]zinc **7** from **8** and **9** [27] in 9.3% yield *(Scheme 2)*. Complex **7** is a mixture of 4 atropisomers having the four possible orientations of the MeO groups relative to the porphyrin plane: $\alpha,\alpha,\alpha,\alpha$, $\alpha,\alpha,\alpha,\beta$, $\alpha,\alpha,\beta,\beta$, and $\alpha,\beta,\alpha,\beta$. Their ratio can be determined from the ^{1}H- and ^{13}C-NMR spectra, *e.g.* the *o*-phenyl H-atoms (H–C(6')) centered at 8.0 ppm display a 17-line (theoretically 24) *m*, originating by superposition of 6 *d*/*d* in the ratio of 1:1:2:2:1:1, in agreement with a 1:4:2:1 distribution of the four atropisomers. Treatment of **7** with HCl yielded the metal-free base **10** which, on addition of an excess of Br_3B, furnished tetrakis(*o*-hydroxyphenyl)porphyrin **11** in 45% yield, also as a mixture of four atropisomers, clearly separated on TLC and HPLC *(Scheme 3)*.

Scheme 3



[a]) For convenience, only one of the four atropisomers is indicated.

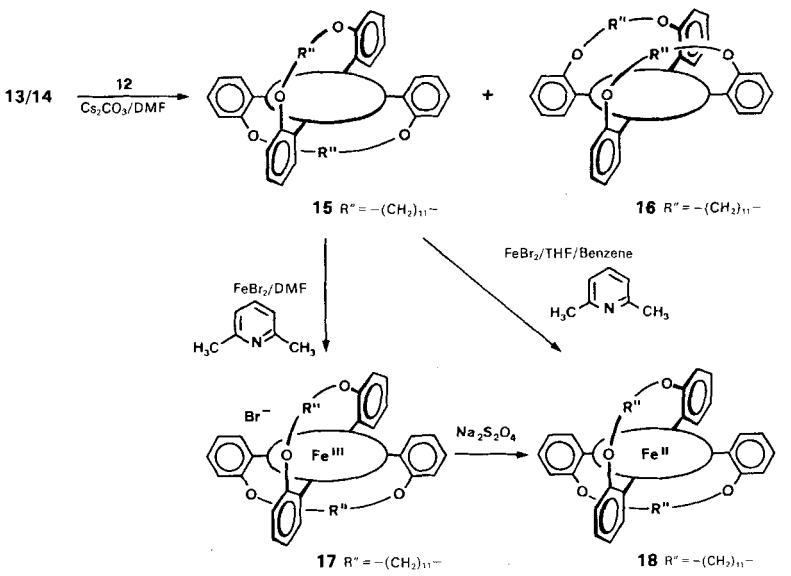
The selective formation of monobridged porphyrin systems presents a major challenge in the synthesis of the enzyme model **6**. Careful investigation of Li_2CO_3, Na_2CO_3, K_2CO_3, and Cs_2CO_3 as reagents in the condensation of the tetraphenol **11** with the dibromide **12** in DMF under high-dilution conditions revealed that Li_2CO_3 was nearly unreactive, K_2CO_3 gave mainly and Cs_2CO_3 exclusively doubly-bridged porphyrins **15** and **16** (see below), whereas Na_2CO_3 was the most successful candidate in yielding a mixture of the monobridged porphyrins **13** and **14** under otherwise identical conditions *(Scheme 3)*. For similar systems, K_2CO_3 has been favoured by *Momenteau et al.* [26]. The crude product from the reaction with Na_2CO_3, containing **13**, **14**, **11**, **15**, and **16**, was purified first by column chromatography in order to separate the least polar doubly-bridged porphyrins **15** and **16**. To separate **13/14** from the starting material **11**, a procedure was used, which has been successfully applied in the tetrakis(*o*-aminophenyl) porphyrin system [28]. The mixture **11/13/14** was isomerised on SiO_2/benzene in order to convert the atropisomers of **11** to α,α,α,α-**11**, and **13** and **14** to the isomers bearing the OH-groups opposite to the bridge-side. α,α,α,α-**11** was easily recovered in 24% yield as the most polar compound by fast chromatography. The mixture **13/14** was then isolated in 62% yield from **11**. The ratio for **13/14** was determined to be 7:3 (^{1}H-NMR), taking into account that **13** has C_{2v} symmetry and consequently enantiotopic H-atoms within the bridging CH_2 groups, whereas **14** has C_s symmetry with diastereotopic H-atoms within the CH_2 groups of the vicinal bridge. Assignment of the individual CH_2 groups is based on ^{1}H-NMR-irradiation experiments performed with each of the more easily separable reference compounds **15** and **16**, *vide infra*.

The yield of 57% for the desired diagonally-monobridged porphyrin **13**, based on converted starting material, documents a remarkable cation-size-dependent selectivity

during ether formation, since **14** and the doubly-bridged porphyrins **15** and **16** are products from competing reactions.

Due to material loss during chromatography, **13/14** were, in general, not separated but converted to **15** and **16** by reaction with the dibromide **12** in the presence of Cs_2CO_3 *(Scheme 4)*. Chromatographic separation afforded pure **15** in 26% yield as reference material for the study of the optimal iron-insertion conditions.

Scheme 4



On addition of $FeBr_2$ to a solution of the ligand **15** in DMF/lutidine, the Fe(III) complex **17** was formed and isolated in 88% yield, exhibiting characteristic MS and UV spectra (λ_{max} 580 and 420 nm). Reduction with $Na_2S_2O_4$ in toluene/H_2O afforded quantitatively the doubly-bridged Fe(II)-porphyrin **18** displaying typical absorption maxima at 541, 445, and 418 nm. In the ^{1}H-NMR spectrum of **18**, the protons of the bridging CH_2 groups appear within an extremely wide range from 24 to −57 ppm, due to the paramagnetism of the complex and accounting for a four-coordinate Fe(II) with intermediate spin state (S = 1) [29]. The same product was obtained by the so called 'direct-insertion' ($FeBr_2$/lutidine, THF/benzene) according to *Collman* and *Groh* [21], omitting the formation of **17**.

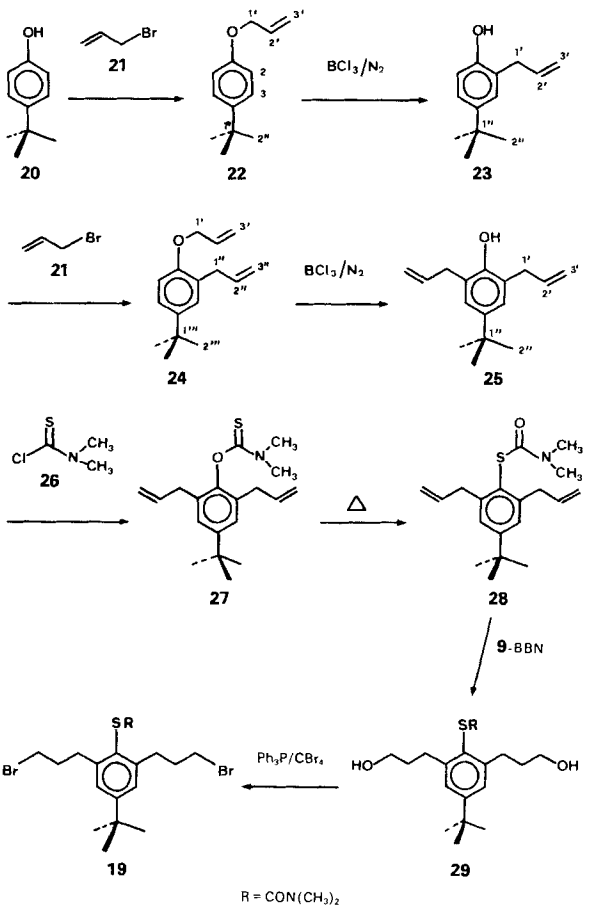
To design a suitable thiol-carrying bridge ready for condensation with the mono-bridged porphyrin **13**, the protected thiophenol derivative **19** was considered to be the molecule of choice for the following reasons *(Scheme 5)*: *1)* The protecting group at the S-atom can only be removed under drastic conditions (KOH/MeOH) and was, therefore, thought to withstand cleavage under conditions where doubly-bridged porphyrins are formed (Cs_2CO_3/DMF, 50°). On the other hand, this new protecting group can easily be introduced in a *Newman-Kwart* rearrangement [30] [31] in which simultaneously an O- and S-atom change positions (see **27**–**28**). *2)* The attachment of the side chains *ortho* to

the S-atom at the benzene ring is expected to favour a proper orientation of the thiophenolate perpendicular to the plane of the porphyrin with little flexibility left. *3*) The *t*-Bu group in *para* position to the S-atom is introduced in order to further restrict motion, *e.g.* disfavour an orientation of the aromatic ring parallel to the porphyrin plane. As a synthetic advantage, the *t*-Bu group leaves no choice for the *Claisen* rearrangement in other than the *ortho* positions.

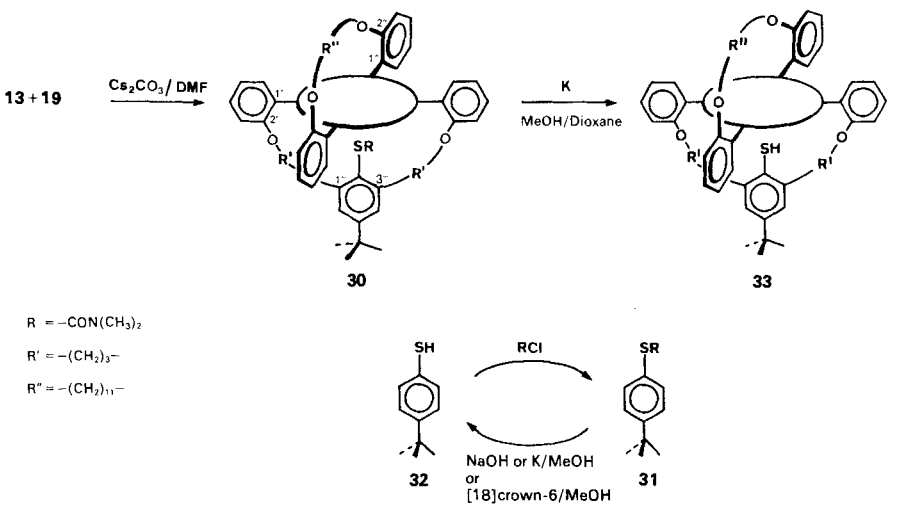
Using a sequence of repetitive allylation/*Claisen* rearrangement [32] [33], commercially available 4-(*tert*-butyl)phenol (**20**) was reacted with **21** and converted *via* **22**–**24** into **25** in 44% yield *(Scheme 5)*. The *o,o'*-diallylphenol **25** was treated with *N,N*-dimethylthiocarbamoyl chlorid (**26**) to give the thiocarbamate **27** which underwent a *Newman-Kwart* rearrangement on heating at 280° to yield the thiophenol derivative **28** in 62% yield. The terminal double bonds of **28** were than modified by standard procedures [34] [35] to furnish the dibromide **19** in 61% yield.

Coupling of the monobridged-porphyrin mixture **13**/**14** with **19** under high-dilution conditions in the presence of Cs_2CO_3 gave, after subsequent column, low-pressure, and

Scheme 5



Scheme 6



thin-layer chromatography, the analytically pure porphyrin **30** (34% yield) with two different bridges stretching diagonally over the opposite faces of the porphyrin chromophore *(Scheme 6)*.

According to CPK models, the porphyrin **30** is chiral. Due to the bulkyness of the protecting group at the S-atom, the 'proximal' bridge is distorted, and the $CON(CH_3)_2$ group is forced into a tilted position relative to the plane of the 'distal' alkane bridge and the porphyrin plane, respectively. Rotation about the S–CO bond is restricted, so that the CH_2 groups and the protons of individual CH_2 groups, which are in **15** homotopic and enantiotopic, respectively, become diastereotopic in **30**.

This is also evident from the ^1H- and ^{13}C-NMR spectra of **30.** Due to different interactions with the ring current of the porphyrin, the two diastereotopic Me groups of the thiocarbamate group appear high-field-shifted

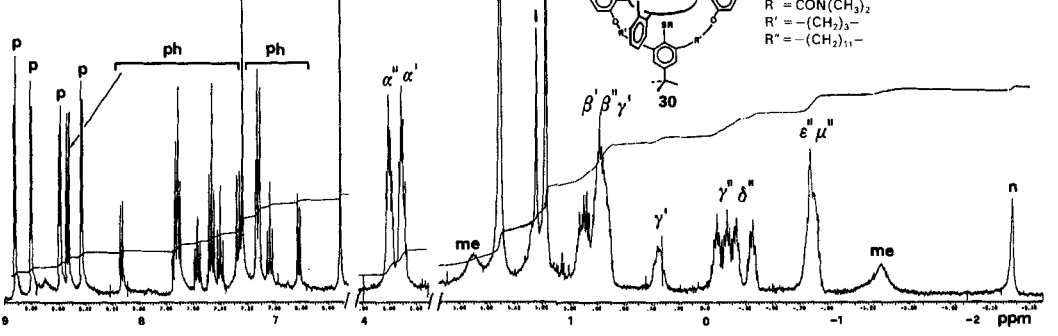


Fig. 1. *^1H-NMR Spectrum* (400 MHz, $CDCl_3$) *of* **30**. CH_2 groups of the bridges are labelled in greek letters, see *Fig. 4;* i: impurity, me: $(CH_3)_2N$; n: NH of pyrrole; p: pyrrole H; ph: *meso*-aryl H; s: solvent; w: H_2O; 2''': thiophenyl H; 2'''': *t*-Bu group.

relative to **19** and separated by 3.0 ppm in the ^{1}H-NMR spectrum of **30**. In contrast, these resonances are only separated by 0.15 ppm in the ^{1}H-NMR spectra of **19** and **29**. The protons of the *meso*-aryl groups appear in 3 sets of signals of relative intensities 1:1:2, and the 4 pyrrole protons adjacent to the *meso*-positions connected by the S-containing bridge display different chemical shifts *(Fig. 1)*.

Deprotection of the severely shielded S-atom in **30** proved to be rather difficult. Most conditions which were suitable for the cleavage of the sterically unhindered thiocarbamate **31** *(Scheme 6)*, prepared as reference material from 4-(*tert*-butyl)thiophenol (**32**), turned out to be unsuccessful when applied to **30**. Only treatment of **30** with a solution of K in MeOH/dioxane 1:1 afforded the thiophenol-carrying ligand **33** in reproducible yields of 50% *(Scheme 6)*. Complete removal of the protecting group was evident from IR, MS, and the signal for the SH at −2.48 ppm in the ^{1}H-NMR, which appears upfield-shifted by 5.8 ppm relative to the SH resonance of **32**. From this ring-current effect, a distance of *ca.* 2.6 Å of the SH to the center of the porphyrin is calculated according to [36], in agreement with the distances measured on CPK and *Dreiding* models. Interestingly, *Collman* and *Groh* [21] reported a chemical shift of 1.36 ppm for SH in the 'sulfur-tail', metal-free ligand corresponding to **5**, which is compatible with a distance of 5–6 Å of SH to the porphyrin center.

Even more remote protons in **33** experience the porphyrin ring current, upfield shifts of 0.95 and 0.39 ppm relative to **19** were observed for the two aromatic protons of the thiophenyl group and for the *t*-Bu group, respectively. The C_s symmetry of **33** is evident from both ^{13}C- and ^{1}H-NMR spectra, the latter showing only two sets of *meso*-aryl protons and, in comparison to **30**, a less complicated signal pattern for the CH_2 groups of the bridges. The interpretation of the resonances, as shown in *Figs. 2* and *3*, is based on irradiation experiments and on comparison with spectra of **15**.

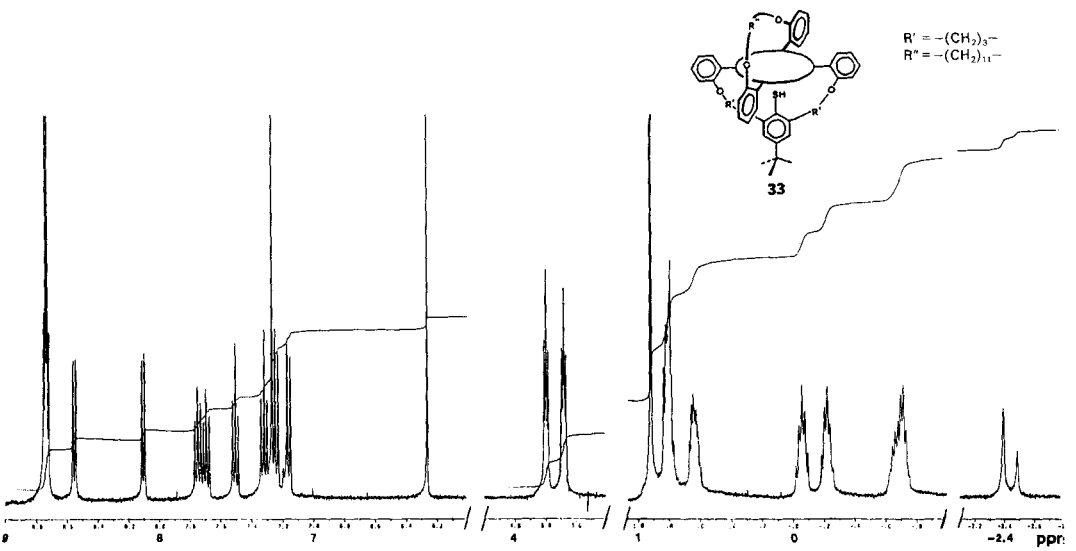


Fig. 2. *^{1}H-NMR Spectrum* (400 MHz, $CDCl_3$) *of* **33**

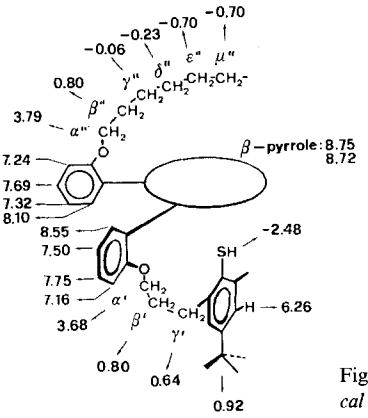
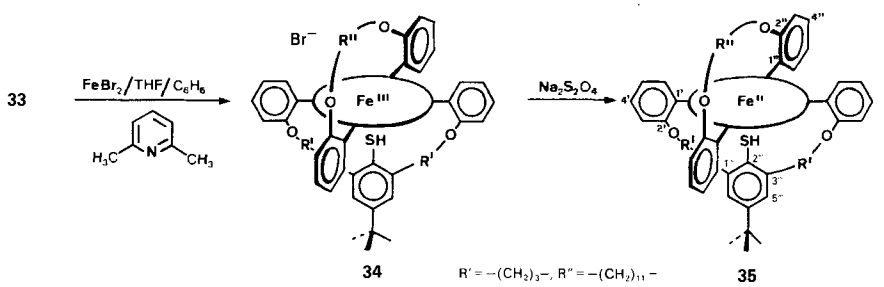


Fig. 3. *Assignment of the* ^{1}*H-NMR chemical shifts* (ppm) *of a partial structure of* **33**

Surprisingly, treatment of the ligand **33** with $FeBr_2$/lutidine in THF/benzene ('direct-insertion' [21]) afforded the Fe(III) complex **34** *(Scheme 7)*, in contrast to experiments with the reference compound **15**. Complex **34** was identified by MS and UV/VIS, displaying characteristic absorption maxima at 673, 568, 513, and 421 nm. Subsequent reduction of **34** with $Na_2S_2O_4$ in toluene/H_2O in the glove box always resulted in a mixture of **34** and a reduced product of faster TLC mobility indicating that, due to the presence of the SH ligand, the reduction potential of **34** is much more negative than that of **17**.

Scheme 7



According to the ^{1}H-NMR spectrum of the reduced species, the desired paramagnetic complex **35** was contaminated by a diamagnetic iron porphyrin displaying a shift range of only 9 ppm to −1 ppm. The structure of this compound is not known yet. Assuming that this diamagnetic complex is different from **35** only due to the presence of a so far unidentified distal ligand, it was reasoned that the reduction has to be carried out in the presence of the strong ligand CO in order to trap **35** as its CO complex. This proved to be a valid approach, since dithionite reduction in a CO atmosphere resulted in the formation of a single product which, after chromatographic separation from unchanged **34**, was shown to be the desired paramagnetic, CO-free Fe(II) complex **35** *(Scheme 7)*.

The reduction of Fe(III) in the presence of the SH group provides the first indication that the design of the enzyme model **6** is correct with respect to the reduced mobility of the S-ligand, since no S–S formation was observed despite the existence of the intramolecu-

lar redox pair Fe(III)/RSH. It is interesting to note that, in the related but sterically less rigid systems of *Battersby et al.* [20] and *Traylor et al.* [22], removal of the protecting group at the S-atom was carried out only after reduction of Fe(III). In the system of *Collman* and *Groh* [21] (see **5**), this problem was circumvented by 'direct insertion' of Fe(II).

The UV spectrum of **35** exhibits characteristic absorptions at 541 and 423 nm in agreement with the published data of protonated **5** [21]. The paramagnetism of **35** is obvious from the ^{1}H-NMR spectrum which extends from 15.8 to −75.9 ppm *(Fig. 4)*. The extremely high-field-shifted resonance of the SH proton at −75.9 ppm indicates, that this proton experiences close contact to the unpaired spin density of Fe(II)-d orbitals.

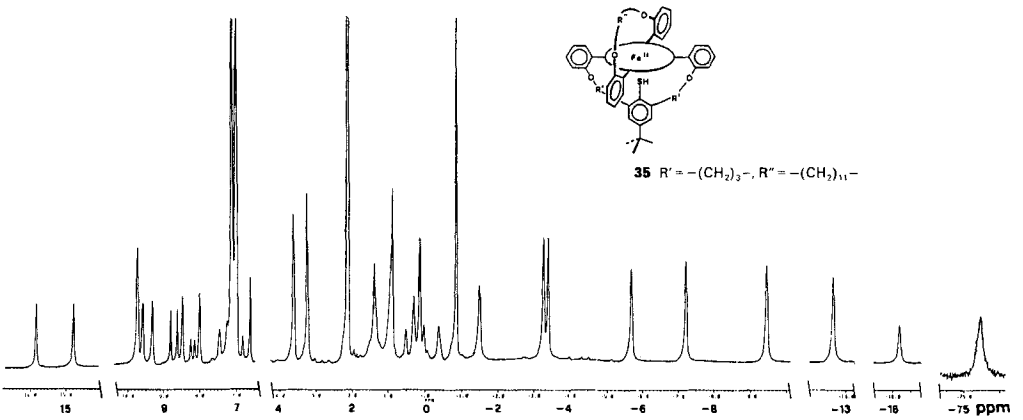


Fig. 4. *^{1}H-NMR Spectrum* (400 MHz, (D_8)toluene) *of* **35**. For clearness, the signal of SH (1 H) is shown enlarged.

The isotropic shifts of the *meso*-aryl protons (downfield) and of the CH_2 groups (upfield) of **35** are essentially dipolar in origin, since both substructures are insulated against spin transmission. The diastereotopic β-pyrrole protons of **35**, however, experience both dipolar and contact shifts leading to very unusual shifts of 8.4 and 11.9 ppm relative to **33** *(Figs. 3* and *5)*. In particular, these values exclude the presence of an Fe(II)

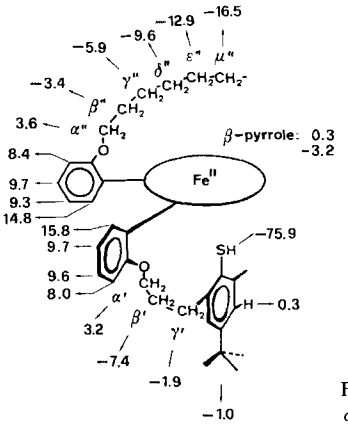


Fig. 5. *Assignment of the ^{1}H-NMR chemical shifts* (ppm) *of a partial structure of* **35**

high-spin complex (S=2), for which β-pyrrole-H resonances of 50 ppm are reported [37]. Separation of the dipolar and contact contributions of the chemical shifts of the β-pyrrole protons of **18** and **35** (see *Fig. 6*) according to *LaMar* and coworkers [38] reveals, that the doubly-alkane-bridged complex **18** ($\Delta\delta_{dip.} = -24.4$ ppm, $\Delta\delta_{cont.} = 28.0$ ppm) displays values close to those of Fe(II)-tetraphenylporphyrin ($\Delta\delta_{dip.} = -21.8$ ppm; $\Delta\delta_{cont.} = 25.9$ ppm), a four-coordinate Fe(II) spin system (S = 1) [38]. In contrast, the β-pyrrole protons of **35** show $\Delta\delta_{dip.} = -8.4$ ppm and $\Delta\delta_{cont.} = 18.6$ ppm, indicating a smaller but dominant π-contact term *(Fig. 6)*. Since these π-contact shifts are only observed in metall porphyrins, which have d_{xz}, d_{yz} unpaired spins but have $d_{x^2-y^2}$ vacant [38] [29], S = 1 is assigned to the doubly-alkane-bridged Fe(II) complex **18**. It also follows that the five-coordinate Fe(II)-porphyrin **35** represents an S = 1 intermediate spin system, considerably disturbed (z^2 orbital presumably destabilised) by the SH ligand close to the metal. The striking difference between **18** and **35** is also reflected in the $(\varkappa_{\parallel} - \varkappa_{\perp})$ values calculated from *Eqn. 1* [38] [39], when angles (θ) and distances (r) are taken from CPK and *Dreiding* models. Omitting protons near $\theta = 54.7°$, the following mean values are determined: $(\varkappa_{\parallel} - \varkappa_{\perp})_{18} = -(6.6 \pm 0.5) \times 10^{-3}$ cm^{-3}mol^{-1} and $(\varkappa_{\parallel} - \varkappa_{\perp})_{35} = -(2.3 \pm 0.3) \times 10^{-3}$ cm^{-3} mol^{-1}.

$$\Delta\delta_{dip.} = -\frac{1}{3N}(\varkappa_{\parallel} - \varkappa_{\perp})\frac{3\cos^2\theta - 1}{r^3} \qquad (1)$$

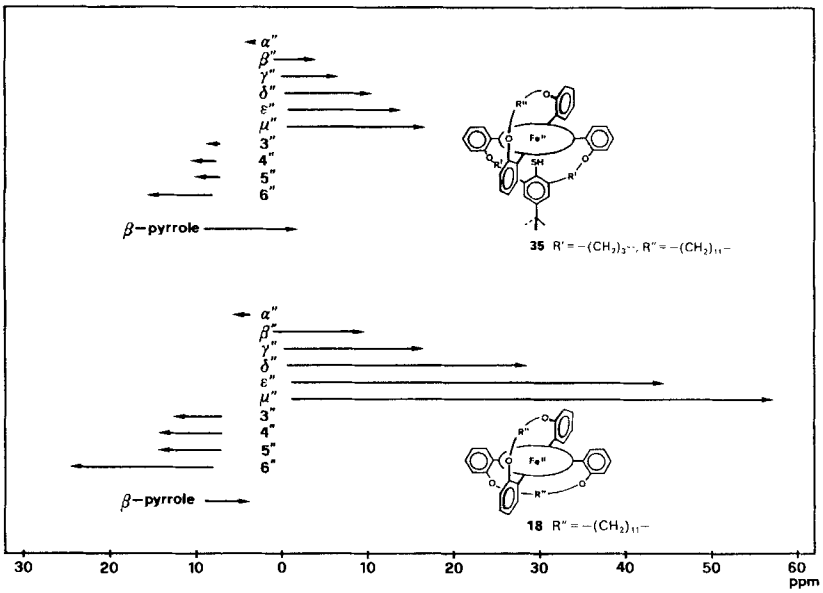
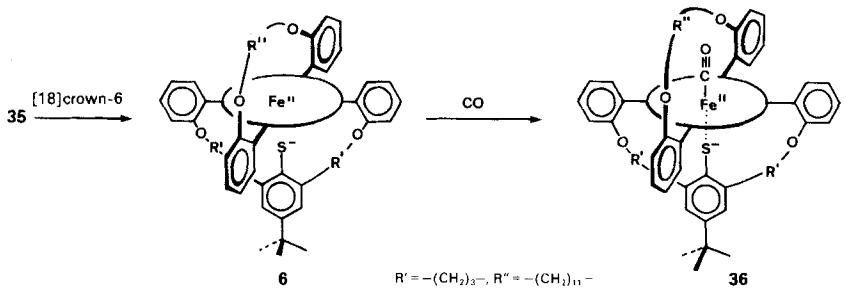


Fig. 6. *Isotropic shifts* (schematic) *of protons of* **18** *and* **35**

ESR and susceptibility measurements have to be carried out in order to interpret the difference between **18** and **35** and to ascribe the ground-state configuration of the S = 1 spin state of **35** [40].

After trying unsuccessfully several bases, *inter alia* $PHNCOCH_3^-K^+$ [21], deprotonation of the severely hindered thiphenol group of the Fe(II)-porphyrin **35** was eventually achieved with KH/toluene in the presence of [18]crown-6 to yield the desired enzym

Scheme 8



model **6** *(Scheme 8)*, displaying a *Soret* band at 425 nm. Since in general native cytochrome P-450 is identified as the hexacoordinate CO complex, CO was injected into a UV sample of **35** to produce reversibly the porphyrin **36**, which shows a split *Soret* band of equal intensities at 403 and 457 nm *(Fig. 7)*.

At present, it is believed that the doubly degenerate single *Soret* band of pentacoordinate metal porphyrins like **6** is a $\pi - \pi^*$ transition [23] [41] [42]. On addition of a strong sixth ligand, this *Soret* band splits into two well separated bands of equal intensity originating from orbital mixing of the degenerate $\pi - \pi^*$ transition with a charge-transfer transition between the π^*-porphyrin orbital and a lone pair p^+ orbital of the thiolate. The

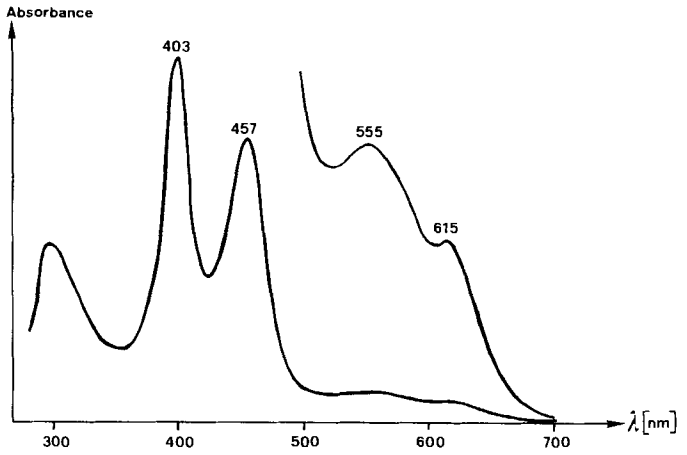


Fig. 7. *UV Spectrum* (toluene) *of* **36**

high-energy component of the split *Soret* band is reported to appear between 350 and 380 nm for different model compounds as well as P-450 isozymes [41] [42] (MO calculations predict 325 nm [23]). The low-energy transitions of the same systems display values between 440 and 480 nm [41] [42] (MO calculations predict 430 nm [23]). Obviously, the high-energy component of the split *Soret* band of the carbonyliron(II) complex **36** is shifted to longer wavelengths by at least 23 nm in comparison to all natural or synthetic systems so far known. This result is not surprising, taking into account that the ArS^- ligand in **36**, for steric reasons, is forced into a position presumably different from native P-450 and model compounds like **5**, in which an energy-minimum orientation can be

adopted. Work is in progress to evaluate the dependence of the splitting of the *Soret* band from the distance and angle of the negative charge at the S-atom relative to the porphyrin plane [40].

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Experimental Part

General. If not otherwise stated, all reagents and solvents were of *'puriss.'* quality and purchased from *Fluka AG* (Buchs) or *Merck*. Et_2O and THF were distilled from $LiAlH_4$. DMF was distilled at 15 Torr and stored over 3-Å molecular sieve *(Union Carbide)*. $CHCl_3$, CH_2Cl_2, hexane, and pentane were purified by passing the solvents through a column of basic Al_2O_3 *(ICN Biomedicals)*. Abs. toluene was obtained by distillation from Na and abs. EtOH by distillation from Mg. All solvents which were used for O_2-sensitive compounds in the glove box were degassed at 0.01 Torr and refilled with Ar. CO (99.97%; *Messer*, Griesheim) was dried over 3-Å molecular sieve. NaH (80% in oil) and KH (65% in oil) were washed three times with abs. hexane (distilled from CaH_2) and stored under Ar before use. Glove box (for handling of O_2-sensitive compounds, in particular the Fe(II)- and Fe(III)-porphyrins): *MECAPLEX G-B 2201*, connected to *MECAPLEX* gas purification equipment; monitoring of O_2 content (10–30 ppm) by an O_2 analyser from *Teledyne Analytical Instruments*. Infusion pump used for slow addition of solutions *via* syringe: *Precidor 5003, INFORS HT*. Sample drying at elevated temp.: *Büchi* oven *TO-50*. Evaporations were performed under reduced pressure (*ca.* 15 Torr) using a *Büchi* rotary evaporator and finally at 0.01 Torr using an *Alcatel* oil pump. TLC: purity control on 5 × 7.5 cm aluminium sheets, SiO_2 *60* F_{254} (precoated; *Merck*); detection by UV_{254} and UV_{366} light or spraying with $KMnO_4$ soln. Prep. TLC on 20 × 20 cm glass plates having 0.25-mm layers of SiO_2 *60* F_{254} (precoated; *Merck*). Column chromatography (CC): SiO_2 *60* (0.063–0.200 mm, 70–230 mesh ASTM; *Merck*), degassed in case of O_2-sensitive compounds at 100°/0.01 Torr for 20 h. Low-pressure liquid chromatography (LPLC): *LiChroprep Si 60;* size B *(Merck)*. GLC: purity control on capillary columns (25 m × 0.25 mm *BP5* or 25 m × 0.32 mm *SE54*). M.p. (uncorrected): *Mettler FP2*. n_D: *WESO*. UV/VIS (nm; $cm^{-1}mM^{-1}$): *Kontron Uvicon 810; Hellma* cell *(117.000)* sealed with *Hellma Subaseal* septum *(011.500)*. IR (cm^{-1}; $CHCl_3$): *Perkin Elmer 297* or *298*. ^{1}H-NMR: *Varian XL-200* (200 MHz) or *Bruker AM-400* (400 MHz); δ in ppm (negative values upfield from TMS) and J in Hz. ^{13}C-NMR, DEPT, and off-resonance spectra: *Varian XL-100* (25.2 MHz) or *XL-200* (50.4 MHz). For a better comparison, the C-atom numbering of all porphyrins is the same: the C-atoms of the pyrrole moieties are characterized by α and β, C-atoms of the bridging C_3-chains by α',β', and γ', C-atoms of the bridging C_{11}-chains by $\alpha'',\beta'',\ldots,\mu''$, C-atoms of the aryl moieties at the *meso*-positions of the porphyrin ring by 1′,2′,... and 1″,2″,..., and C-atoms of the S-substituted aryl moiety by 1‴,2‴,... If not otherwise stated, spectra were recorded at 25°. MS (*m/z* (rel. intensity $\geq$ 5%, if not otherwise stated)): *Varian MAT 112S* (70 eV) or *MAT 711* (70 eV).

[5,10,15,20-Tetrakis(2-methoxyphenyl)porphyrinato]zinc (**7**)[2]. To a mixture of *o-methoxybenzaldehyde* (**9**; 68.1 g, 500 mmol) and Zn $(OAc)_2 \cdot 2\,H_2O$ (27.4 g, 125 mmol) in propionic acid (2.5 l), *pyrrole* (**8**; 33.6 g, 500 mmol) was added at 100° within 1 h under vigorous stirring [27]. The resulting dark soln. was refluxed for further 4 h and than kept at 4° over night in order to precipitate the products. After filtration, the residue was washed with cold propionic acid (500 ml) and EtOH (1 l), dissolved in $CHCl_3$ (1.5 l), and filtered. Removal of the solvents at 15 and 0.01 Torr afforded 18.1 g of a dark blue solid, containing **7** and the corresponding chlorin. The mixture was dissolved in $CHCl_3$ (200 ml)/pyridin (20 ml) at 45° and treated with an excess of 4,5-dichloro-3,6-dioxo-1,4-cyclohexadiene-1,2-dicarbonitril (DDQ), suspended in $CHCl_3$. After complete oxidation (monitoring by the disappearance of the 626-nm absorption of the chlorin), the soln. was filtered and evaporated, and the solid residue subjected to CC on SiO_2 (400 g, 6.5 × 30 cm) with $CHCl_3$/MeOH 95:5. The blue-violet **7** (9.30 g) was isolated in 9.3% yield and crystallised from CH_2Cl_2/MeOH to afford an anal. pure, purple, microcrystalline sample. TLC (SiO_2,

[2]) The synthesis of this compound has already been published under the references given. Our modifications improved the experimental procedure; moreover, the complete spectroscopical data and interpretations are presented.

$CHCl_3/Et_2O$ 9:1): R_f 0.20 ($\alpha,\alpha,\alpha,\alpha$-**T**), 0.42 ($\alpha,\alpha,\alpha,\beta$-**T**), 0.54 ($\alpha,\alpha,\beta,\beta$-**T**), 0.56 ($\alpha,\beta,\alpha,\beta$-**T**); rel. int.: 1:4:2:1. M.p. > 300°. UV/VIS ($CHCl_3$): 647 (sh, 0.17), 581 (sh, 2.1), 548 (16.5), 509 (2.4), 483 (sh, 1.4), 420 (425), 398 (31.3), 346 (sh, 8.7), 309 (10.1). IR (KBr): 3060*w*, 3000*w*, 2930*w*, 2830*w*, 1600*m*, 1590*w*, 1520*w*, 1490*s*, 1460*m*, 1450*m*, 1435*m*, 1340*m*, 1290*w*, 1275*w*, 1250*s*, 1220*m*, 1200*m*, 1180*w*, 1160*w*, 1120*m*, 1065*m*, 1050*m*, 1040*w*, 1025*m*, 1010*m*, 995*s*, 855*w*, 830*w*, 800*s*, 755*s*, 730*m*, 720*m*, 700*m*, 650*m*, 630*w*. ^{1}H-NMR (400 MHz, $CDCl_3$): 8.81–8.79 (*m*, 8 H–C(β) of pyrrole); 8.05, 8.04, 8.02, 8.01, 8.00, 7.98 (6 *dd*, ^3J (5',6') = 7.0, ^4J (4',6') = 1.7, rel. int. 1:1:2:2:1:1, 4 H–C(6')); 7.74 (*dd*, ^3J (3',4') ≈ ^3J (4',5') ≈ 8, 4 H–C(4')); 7.36–7.29 (*m*, 4 H–C(3'), 4 H–C(5')); 3.58–3.55 (*m*, 4 CH_3). ^{13}C-NMR (50 MHz, $CDCl_3$): 159.72, 159.65, 159.60, 159.55 (C(2')); 149.93 (C(α) of pyrrole); 135.50, 135.45, 135.34 (C(6')); 132.74 (C(1')); 130.90 (C(β) of pyrrole); 129.09 (C(4')); 119.14, 119.09, 119.01 (C(5')); 115.72 (C(*meso*)); 111.08, 110.97, 110.88 (C(3')); 55.94 (CH_3). MS: 802 (7), 801 (26), 800 (49, [*M*(^{68}Zn)]$^{+\cdot}$), 799 (44), 798 (77, [*M*(^{66}Zn)]$^{+\cdot}$), 797 (58), 796 (100, [*M*(^{64}Zn)]$^{+\cdot}$), 400 (6, [*M*(^{68}Zn)]$^{2+}$), 399 (10, [*M*(^{66}Zn)]$^{2+}$), 398 (11, [*M*(^{64}Zn)]$^{2+}$). Anal. calc. for $C_{48}H_{36}N_4O_4Zn$ (798.22): C 72.23, H 4.55, N 7.02, Zn 8.19; found: C 72.17, H 4.73, N 7.25, Zn 7.76.

5,10,15,20-Tetrakis(2-methoxyphenyl)porphyrin (**10**)[2]. A soln. of **7** (9.30 g, 11.7 mmol) in 400 ml of $CHCl_3$ was treated under vigorous shaking, twice with 400 ml of 18% HCl soln., once with H_2O (400 ml) and 3 times with 400 ml of sat. $NaHCO_3$ soln. Subsequent drying (Na_2SO_4) of the org. layer and evaporation yielded **10** (6.06 g, 71%) [27]. Crystallisation from CH_2Cl_2/MeOH furnished an anal. pure, deep purple solid. TLC (SiO_2, $CHCl_3/Et_2O$ 95:5): R_f 0.39 ($\alpha,\alpha,\alpha,\alpha$-**10**), 0.56 ($\alpha,\alpha,\alpha,\beta$-**10**), and 0.64 ($\alpha,\alpha,\beta,\beta$-**10** and $\alpha,\beta,\alpha,\beta$-**10**); rel. int.: 1:4:(2 + 1). M.p. > 300°. UV/VIS ($CHCl_3$): 645 (2.0), 590 (5.6), 547 (5.2), 514 (18.9), 483 (3.0), 419 (426), 401 (sh, 79.3), 370 (21.7), 350 (sh, 18.9), 304 (14.3). IR (KBr): 3320*w*, 3060*w*, 3020*w*, 3000*w*, 2940*m*, 2840*m*, 2710*w*, 2540*w*, 2360*w*, 2040*w* (br.), 1810*w* (br.), 1600*m*, 1580*m*, 1560*w*, 1490*s*, 1465*s*, 1435*s*, 1405*w*, 1350*m*, 1290*m*, 1270*m*, 1250*s*, 1215*m*, 1205*m*, 1180*m*, 1160*m*, 1120*m*, 1050*m*, 1025*s*, 990*m*, 980*m*, 970*s*, 880*w*, 855*w*, 825*w*, 800*s*, 755*s*, 730*m*, 650*m*. ^{1}H-NMR (400 MHz, $CDCl_3$): 8.73 (s, 8 H–C(β) of pyrrole); 8.06, 8.00, 7.95 (3 *d*, ^3J (5',6') = 6.8, rel. int. 1:2:1, 4 H–C(6')); 7.75 (*dd*, ^3J (3',4') ≈ ^3J (4',5') ≈ 7.5, 4 H–C(4')); 7.38–7.28 (*m*, H–C(3'), 4 H–C(5')); 3.61, 3.58, 3.55 (3 *s*, rel. int. 1:2:1, 4 CH_3); –2.61 (br. *s*, 2 NH). ^{13}C-NMR (50 MHz, $CDCl_3$): 159.58, 159.53 (C(2')); 147 (v. br., C(α) of pyrrole); 135.73, 135.68, 135.64 (C(6')); 131.39 (C(1')); 130.5 (br., C(β) of pyrrole); 129.65 (C(4')); 119.38 (C(5')); 115.51 (C(*meso*)); 111.06 (C(3')); 55.90 (CH_3). MS: 736 (18), 735 (56), 734 (100, $M^{+\cdot}$), 367.5 (7), 367 (12, M^{2+}). Anal. calc. for $C_{48}H_{38}N_4O_4$ (734.85): C 78.46, H 5.21, N 7.62; found: C 78.41, H 5.38, N 7.45.

5,10,15,20-Tetrakis(2-hydroxyphenyl)porphyrin (**11**)[2]. A suspension of **10** (13.0 g, 17.7 mmol) in CH_2Cl_2 (300 ml) was slowly treated with a soln. of BBr_3 (26.6 g; 106 mmol) in $CHCl_3$ (250 ml) at –50° under Ar. After stirring for further 1.5 h at –50°, the soln. was allowed to reach 25° over night and subsequently treated with $CHCl_3$ (700 ml)/H_2O (300 ml) in order to precipitate the porphyrins. From the resulting solid, **11** was extracted into $CHCl_3$ by repetitive, vigorous shaking in $CHCl_3$ (1% MeOH)/sat. $NaHCO_3$ soln. The combined org. layers were washed again with sat. $NaHCO_3$ soln. and H_2O, dried (Na_2SO_4), and finally evaporated: 6.3 g of crude **11**. CC on SiO_2 (300 g, 9.5 × 9.5 cm) with $CHCl_3$/MeOH 95:5 yielded **11** (5.37 g, 45%) as a mixture of atropisomers from the second intensely colored band. Anal. pure material was obtained by adding hexane to a soln. of **11** in CH_2Cl_2/MeOH 4:1 and washing the resulting precipitate with CH_2Cl_2/hexane: microcristalline, violet-blue powder, which is slightly hygroscopic. TLC (SiO_2, $CHCl_3$/MeOH 95:5): R_f 0.11 ($\alpha,\alpha,\alpha,\alpha$-**11**), 0.30 ($\alpha,\alpha,\alpha,\beta$-**11**), 0.42 ($\alpha,\alpha,\beta,\beta$-**11**), and 0.48 ($\alpha,\beta,\alpha,\beta$-**11**); rel. int. 1:4:2:1. M.p. > 300°. UV/VIS ($CHCl_3$): 643 (1.4), 587 (6.0), 547 (4.6), 513 (18.3), 482 (sh, 3.3), 418 (334), 399 (sh, 81.3), 372 (sh, 26.5), 350 (sh, 21.7), 310 (sh, 14.4). IR (KBr): 3700–2900*s* (v.br.), 2700*w*, 2610*w*, 2530*w*, 1815*w* (br.), 1610*m*, 1580*m*, 1490*s*, 1475*s*, 1450*s*, 1400*m*, 1350*m*, 1330*m*, 1290*s*, 1220*s*, 1170*s*, 1150*s*, 1100*m*, 1040*m*, 995*m*, 980*m*, 970*s*, 885*w*, 860*w*, 815*s*, 800*s*, 755*s*, 725*s*, 650*m*. ^{1}H-NMR (400 MHz, $CDCl_3$): 8.92–8.87 (*m*, 8 H–C(β) of pyrrole); 7.99–7.91 (*m*, 4 H–C(6')); 7.75–7.66 (*m*, 4 H–C(4')); 7.37–7.27 (*m*, 4 H–C(3'), 4 H–C(5')), 4.92 (br. *s*, 4 OH); –2.76 (br. *s*, 2 NH). ^{13}C-NMR (50 MHz, $CDCl_3/CD_3OD$ 9:1)[3]: 156.54, 156.44 C(2')); 135.30 (C(6')); 130.22 (C(4')); 128.25, 128.18, 128.13 (C(1')); 118.87 (C(5')); 115.63 (C(3')); 115.19 (C(*meso*)). MS (peaks > 7%): 680 (12), 679 (47), 678 (100, $M^{+\cdot}$), 677 (23), 585 (9, [M – (C_6H_4)OH]$^+$), 339.5 (9), 339 (17, M^{2+}). Anal. calc. for $C_{44}H_{30}N_4O_4 \cdot 1.5\ H_2O$ (678.75 + 27.02): C 74.88, H 4.71, N 7.94; found: C 75.21, H 4.98, N 7.46.

5,15-Bis(2-hydroxyphenyl)-10,20-(undecamethylenedioxydi-2,1-phenylene)porphyrin (**13**) *and 5,10-Bis(2-hydroxyphenyl)-15,20-(undecamethylenedioxydi-2,1-phenylene)porphyrin* (**14**). To a soln. of **11** (732 mg, 1.08 mmol) in DMF (150 ml) under Ar at 100°, dry Na_2CO_3 (1.72 g, 16.2 mmol) was added. Then, a soln. of *1,11-dibromoundecane* (**12**; 373 mg, 1.19 mmol) in DMF (20 ml) was injected by syringe within 15 h using an infusion pump. The soln.

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[3]) ^{13}C-NMR signals of C(α) and C(β) of the pyrrole moieties are not detectable at 25°; at 50°, the C(α)'s are still not observed, however, the C(β)'s appear at 131.3 ppm.

was stirred for further 90 min at 100°, then cooled to 25°, and transferred into 500 ml of $CHCl_3$/sat. NH_4Cl soln. 1:1. The org. layer was separated, washed once with sat. NH_4Cl soln., twice with H_2O, then dried (Na_2SO_4), evaporated at 15 Torr and finally at 0.01 Torr to afford 1.01 g of crude products. Gradient CC on SiO_2 (150 g, 4 × 30 cm) with toluene/hexane 3:2 gave 2 fractions, containing **15** (320 mg, 30%) and **16** (*ca.* 1 mg). Subsequent elution with $CHCl_3$/MeOH 95:5 afforded 778 mg of **13/14**, contaminated by **11**. The mixture **11/13/14** was heated in 20 ml of benzene for 1 h at 50° under Ar in the presence of 5 g of SiO_2. Fast CC on SiO_2 (90 g, 2.5 × 37 cm) with toluene, followed by elution with $CHCl_3$/MeOH 97:3 yielded 558 mg (62%) of **13/14** (7:3; by ^{1}H-NMR). Final elution with acetone/Et_2O 1:1 gave pure $\alpha,\alpha,\alpha,\alpha$-**11** (175 mg, 24%). Separation of **13/14** was achieved by converting these isomers into the more polar α,α-atropisomers as described above. Fast CC on SiO_2 with $CHCl_3$/MeOH 98:2 followed by TLC (SiO_2, $CHCl_3$/MeOH 99:1) of the most polar fraction resulted in 2 well separated bands on TLC, from which **13** (R_f 0.43) and **14** (R_f 0.32) were isolated. ^{1}H-NMR (400 MHz, $CDCl_3$) of **13**[4]: 8.85, 8.83 (2 *d*, ^3J = 5.0, *AB*, 8 H–C(β) of pyrrole); 8.15 (*dd*, ^3J(5′,6′) = 7.4, ^4J(4′,6′) = 1.6, 2 H–C(6′)); 8.12 (*dd*, ^3J(5″,6″) = 7.4, ^4J(4″,6″) = 1.6, 2 H–C(6″)); 7.76 (*ddd*, ^3J(3′,4′) = 8.3, ^3J(4′,5′) = 7.5, ^4J(4′,6′) = 1.6, 2 H–C(4′)); 7.72 (*ddd*, ^3J(3″,4″) = 8.3, ^3J(4″,5″) = 7.5, ^4J(4″,6″) = 1.6, 2 H–C(4″)); 7.40 (*ddd*, ^3J(4′,5′) = 7.5, ^3J(5′,6′) = 7.4, ^4J(3′,5′) = 1.0, 2 H–C(5′)); 7.37 (*ddd*, ^3J(4″,5″) = 7.5, ^3J(5″,6″) = 7.4, ^4J(3″,5″) = 1.0, 2 H–C(5″)); 7.33 (*dd*, ^3J(3′,4′) = 8.3, ^4J(3′,5′) = 1.0, 2 H–C(3′)); 7.30 (*dd*, ^3J(3″,4″) = 8.3, ^4J(3″,5″) = 1.0, 2 H–C(3″)); 4.82 (br. *s*, 2 OH, exchange with D_2O); 3.84 (*t*, *J* = 5.3, 4 H–C(α″)); 0.86–0.76 (*m*, 4 H–C(β″)); –0.13 to –0.24 (*m*, 4 H–C(γ″)); –0.44 to –0.54 (*m*, 4 H–C(δ″)); –1.06 to –1.15 (*m*, 4 H–C(ε″)); –1.18 to –1.26 (*m*, 2 H–C(μ″)); –2.68 (br. *s*, 2 NH). ^{1}H-NMR (400 MHz, $CDCl_3$) of **14**[4]: 8.90–8.80 (*m*, 8 H–C(β) of pyrrole); 8.02 (*dd*, ^3J(5′,6′) = 7.4, ^4J(4′,6′) = 1.8, 2 H–C(6′)); 8.00 (*dd*, ^3J(5″,6″) = 7.4, ^4J(4″,6″) = 1.8, 2 H–C(6″)); 7.75 (*ddd*, ^3J(3′,4′) = 8.0, ^3J(4′,5′) = 7.5, ^4J(4′,6′) = 1.8, 2 H–C(4′)); 7.72 (*ddd*, ^3J(3″,4″) = 8.0, ^3J(4″,5″) = 7.5, ^4J(4″,6″) = 1.8, 2 H–C(4″)); 7.37 (*ddd*, ^3J(4′,5′) = 7.5, ^3J(5′,6′) = 7.4, ^4J(3′,5′) = 1.0, 2 H–C(5′)); 7.36 (*dd*, ^3J(3′,4′) = 8.0, ^4J(3′,5′) = 1.0, 2 H–C(3′)); 7.34 (*dd*, ^3J(3″,4″) = 8.0, ^4J(3″,5″) = 1.0, 2 H–C(3″)); 7.33 (*ddd*, ^3J(4″,5″) = 7.5, ^3J(5″,6″) = 7.4, ^4J(3″,5″) = 1.0, 2 H–C(5″)); 5.03 (br. *s*, 2 OH); 3.94–3.82 (*m*, 4 H–(α″)); 1.00 to –0.90 (*m*, 4 H–C(β″)); 0.11 to –0.01 (*m*, 2 H–C(γ″)); –0.10 to –0.22 (*m*, 2 H–C(γ″)); –0.38 to –0.52 (*m*, 4 H–C(δ″)); –0.48 to –0.60 (*m*, 2 H–C(ε″)); –0.95 to –1.07 (*m*, 2 H–C(ε″)); –1.75 (br. *s*, H–C(μ″)); –1.96 (br. *s*, H–C(μ″)); –2.69 (br. *s*, 2 NH). MS (**13/14** 7:3): 832 (21), 831 (52), 830 (100, $M^{+\cdot}$), 415 (5, M^{2+}).

5,15:10,20-Bis(undecamethylenedioxydi-2,1-phenylene)porphyrin (**15**) *and* cis-*5,20:10,15-Bis(undecamethylenedioxydi-2,1-phenylene)porphyrin* (**16**)[2]. To **13/14** (7:3; 500 mg, 0.602 mmol) in DMF (25 ml) under Ar at 50° and 2.94 g Cs_2CO_3 (9.02 mmol), a soln. of 227 mg (0.723 mmol) of **12** in 5 ml of DMF was injected within 2 h *via* septum and the resulting mixture stirred for further 3 h at 50°. Isolation by extraction from 100 ml of sat. NH_4Cl soln. with 150 ml of $CHCl_3$, washing of the combined org. layers with 100 ml of sat. NH_4Cl soln. and H_2O (100 ml), drying (Na_2SO_4), and final evaporation (0.01 Torr) gave 525 mg crude product. CC on SiO_2 (60 g, 2.5 × 34 cm) with toluene/hexane 3:2 furnished 2 main red-violet bands. From the first eluting band, **15** (207 mg, 26%) and from the second **16** (15.0 mg, 2.5%) was isolated as anal. pure samples, which were both recrystallised from CH_2Cl_2/MeOH. Porphyrins **15** and **16** were also prepared directly from **11** in 23% yield using a 4-fold excess of **12** and Cs_2CO_3. **15**: M.p. > 300°. UV/VIS ($CHCl_3$): 680 (sh, 0.15), 647 (2.2), 592 (6.0), 547 (6.0), 514 (20.0), 482 (3.5), 419 (416), 402 (sh, 79.9), 372 (22.5), 356 (19.4), 303 (14.0). IR (KBr): 2920*s*, 2850*s*, 1800*w* (br.), 1595*w*, 1580*w*, 1490*s*, 1465*m*, 1450*s*, 1350*w*, 1270*m*, 1250*s*, 1230*m*, 1185*w*, 1160*w*, 1110*m*, 1050*m*, 990*w*, 980*w*, 965*s*, 800*s*, 750*s*, 730*m*, 710*w*, 650*w*. ^{1}H-NMR (400 MHz, $CDCl_3$): 8.74 (*s*, 8 H–C(β) of pyrrole); 8.22 (*dd*, ^3J(5′,6′) = 7.4, ^4J(4′,6′) = 1.7, 4 H–C(6′)); 7.73 (*ddd*, ^3J(3′,4′) = ^3J(4′,5′) = 7.4, ^4J(4′,6′) = 1.7, 4 H–C(4′)); 7.39 (*dd*, ^3J(4′,5′) = ^3J(5′,6′) = 7.4, 4 H–C(5′)); 7.27 (*d*, ^3J(3′,4′) = 7.4, 4 H–C(3′)); 3.79 (*t*, *J* = 5.2, 8 H–C(α″)); 0.81–0.72 (*m*, 8 H–C(β″)); –0.12 to –0.21 (*m*, 8 H–C(γ″)); –0.36 to –0.45 (*m*, 8 H–C(δ″)); –0.92 to –1.03 (*m*, 8 H–C(ε″) and 4 H–C(μ″))[5]; –2.56 (br. *s*, 2 NH. ^{13}C-NMR (200 MHz, $CDCl_3$): 159.59 (C(2′)); ~ 147 (v.br., C(α) of pyrrole); 135.13 (C(6′)); 132.40 (C(1′)); 130.4 (br., C(β) of pyrrole); 129.49 (C(4′)); 119.47 (C(5′)); 115.55 (C(*meso*)); 113.02 (C(3′)); 69.27 (C(α″)); 28.49, 27.57, 27.50, 25.35 (C(β″), C(γ″), C(δ″), C(ε″)); 26.87 (C(μ″)). MS: 983 (9), 982 (100, $M^{+\cdot}$), 491 (9, M^{2+}). Anal. calc. for $C_{66}H_{70}N_4O_4$ (983.32): C 80.62, H 7.18, N 5.70; found: C 80.67, H 7.37, N 5.91.

16: M.p. 298–300°. UV/VIS (toluene): 648 (2.5), 592 (6.0), 547 (6.2), 515 (20.2), 483 (3.4), 420 (416), 405 (sh, 82.7), 373 (23.3), 348 (sh, 19.2), 305 (14.9). IR (KBr): 2920*s*, 2850*m*, 1595*w*, 1580*w*, 1490*m*, 1470*m*, 1445*s*, 1350*w*, 1285*w*, 1250*s*, 1210*w*, 1180*w*, 1160*w*, 1115*m*, 1045*w*, 990*w*, 980*w*, 965*s*, 800*s*, 750*s*, 730*m*, 650*w*. ^{1}H-NMR (400 MHz, $CDCl_3$): 8.70 (*s*, 8 H–C(β) of pyrrole); 7.88 (*dd*, ^3J(5′,6′) = 7.4, ^4J(4′,6′) = 1.7, 4 H–C(6′)); 7.70 (*ddd*, ^3J(3′,4′) = 8.3, ^3J(4′,5′) = 7.5, ^4J(4′,6′) = 1.7, 4 H–C(4′)); 7.33 (*dd*, ^3J(3′,4′) = 8.3 ^4J(3′,5′) = 0.9, 4 H–C(3′)); 7.28

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[4]) The protons of the *meso*-aryl moieties of **13** and **14** cannot be assigned; *i.e.* primed and doubly primed numbers may be interchanged.

[5]) The resonances of H–C(μ″) and H–C(ε″) are separated at 0°.

(*ddd*, $^3J(4',5') = 7.5$, $^3J(5',6') = 7.4$, $^4J(3',5') = 0.9$, 4 H–C(5')); 4.00–3.95 (*m*, 8 H–C(α'')); 1.20–1.05 (*m*, 8 H–C(β'')); 0.37–0.24 (*m*, 4 H–C(γ'')); 0.30–0.17 (*m*, 4 H–C(γ'')); –0.15 to –0.27 (*m*, 4 H–C(δ''), 4 H–C(ε'')); –0.23 to –0.35 (*m*, 4 H–C(δ'')); –0.53 to –0.65 (*m*, 4 H–C(ε'')); –1.37 to –1.49 (*m*, (br. *s*), 2 H–C(μ'')); –1.56 to –1.68 (*m* (br. *s*), 2 H–C(μ'')); –2.63 (br. *s*, 2 NH). ^{13}C-NMR (50 MHz, $CDCl_3$): 158.84 (C(2')); 136.45 (C(6')); 132.10 (C(1')); 131.06 (br., C(β) of pyrrole); 129.44 (C(4')); 119.45 (C(5')); 115.73 (C(*meso*)); 112.69 (C(3')); 69.46 (C(α'')); 28.38, 27.56, 27.17, 25.41 (C(β''), C(γ''), C(δ''), C(ε'')); 25.86 (C(μ'')). MS: 985 (10), 984 (29), 983 (72), 982 (100, $M^{+\cdot}$), 981 (11), 980 (7), 831 (6), 830 (7), 829 (8, $[M - (CH_2)_{11}+H]^+$). Anal. calc. for $C_{66}H_{70}N_4O_4$ (983.32): C 80.62, H 7.18, N 5.70; found: C 80.60, H 7.05, N 5.70.

β-Bromo[5,15:10,20-bis(undecamethylenedioxydi-2,1-phenylene)porphyrinato]iron(III) (**17**). To a refluxing soln. of **15** (200 mg, 0.203 mmol) in DMF (15 ml) 0.4 ml of 2,6-dimethylpyridine and 350 mg of $FeBr_2$ (1.62 mmol) were added. The mixture was heated for further 1.5 h, when **15** had been consumed (TLC (SiO_2), toluene, R_f (**15**) 0.58). Evaporation at 0.01 Torr furnished a dark-brown residue which was suspended in $CHCl_3$. Shaking of the org. layer twice with 150 ml of H_2O and twice with 150 ml of 7% aq. HBr soln, drying (Na_2SO_4), and evaporation furnished crude **17**. CC on SiO_2 (10 g, 1.4 × 40 cm; $CHCl_3$/MeOH 95:5) afforded a single brown-red fraction, from which **17** (200 mg, 88%) was isolated spectroscopically pure. R_f 0.77 (SiO_2, $CHCl_3$/MeOH 95:5). M.p. 185–188° (toluene). UV (toluene): 688 (sh, 1.8), 626 (sh, 3.3), 580 (7.3), 500 (sh, 12.9), 420.0 (106), 350 (32.0). IR (KBr): 3050*w*, 2920*s*, 2850*s*, 1810*w* (br.), 1725*w*, 1600*m*, 1580*m*, 1530*w*, 1495*m*, 1465*m*, 1445*s*, 1380*w*, 1330*m*, 1290*m*, 1260*s*, 1230*m*, 1200*m*, 1160*m*, 1120, 1070*m*, 1050*m*, 1000*s*, 830*w*, 800*s*, 755*s*, 720*m*, 655*m*. MS: 1039 (10), 1038 (32), 1037 (70), 1036 (100, $[M - Br]^+$), 1035 (15), 103 (16), 884 (6, $[M - Br(CH_2)_{11}+H_2]^+$), 731 (6), 730 (8, $[M - Br(CH_2)_{22} + H_2]^+$), 518 (6, $[M - Br]^{2+}$).

5,15:10,20-Bis(undecamethylenedioxydi-2,1-phenylene)porphyrinato]iron(II) (**18**). A soln. of **17** (17 mg, 0.015 mmol) in 1.5 ml of (D_8)toluene was stirred at 25° in the presence of 1.5 ml of 1M $Na_2S_2O_4$ in D_2O. The reduction was complete after 1 h (TLC (SiO_2, toluene), R_f (**17**) 0.03 (brown spot), R_f (**18**) 0.55 (orange spot)). The org. layer was separated, filtered through cotton, and directly submitted to spectroscopical analysis.

The same complex **18** was obtained in almost quant. yield by 'direct insertion' [21] on heating **15** (20 mg, 0.02 mmol) in THF/benzene 1:1 (10 ml) in the presence of 50 mg of dimethylpyridine and 25 mg of $FeBr_2$ for 15 h. UV/VIS (toluene): 541 (14%), 445 (100%), 418 (100%); 400 (sh, 65%), 343 (21%), 310 (17%). ^{1}H-NMR (400 MHz, (D_8)toluene): 23.68 (*s*, 4 H–C(6')); 13.57 (*s*, 4 H–C(5')); 13.38 (*s*, 4 H–C(4')); 12.42 (*s*, 4 H–C(3')); 5.40 (*s*, 8 H–C(α'')); 5.17 (*s*, 8 H–C(β) of pyrrole); –8.64 (*s*, 8 H–C(β'')); –16.03 (*s*, 8 H–C(γ'')); –28.26 (*s*, 8 H–C(δ'')); –44.00 (*s*, 8 H–C(ε'')); –57.17 (*s*, 4 H–C(μ'')).

*4-(*tert*-Butyl)phenyl Allyl Ether* (**22**)[2]. A soln. of *4-(*tert*-butyl)phenol* (**20**, 22.5 g, 150 mmol) in EtOH (40 ml) was added to a stirred soln. of Na (3.80 g, 165 mmol) in EtOH (120 ml) at 25°. After further 15 min stirring, allylbromide **21**; 20.0 g, 165 mmol) was added neat within 45 min. The mixture was stirred at 25° for 1 h and heated to 70° for 1 h. The solvent volume was reduced by evaporation at 15 Torr and poured into H_2O (300 ml). After extraction (3 times) with 150 ml of Et_2O, the combined org. layers were washed twice with 100 ml of 10% NaOH soln., 3 times with 100 ml of H_2O, dried (Na_2SO_4), and evaporated to afford 26.4 g of crude product which was distilled over a 10-cm *Vigreux* column at 120°/15 Torr to give 24.9 g (87%) of **22** (96.2% pure by GLC) [43] [44]. $n_D^{24} = 1.5058$. UV($CHCl_3$): 282 (8.2), 275 (9.8), 239 (7.9). IR ($CHCl_3$): 3010*w*, 2970*s*, 2910*w*, 2880*w*, 1610*w*, 1570*m*, 1510*s*, 1500*m*, 1240–1200*s*, 1190*s*, 1120*s*, 1120*m*, 1020*m*, 1000*m*, 930*m*, 830*s*. ^{1}H-NMR (200 MHz, $CDCl_3$): 7.38–7.28 (*m*, H–C(3), H–C(5)); 6.95–6.85 (*m*, H–C(2), H–C(6)); 6.08 (*ddt*, $^3J(2',3'a) = 17.3$, $^3J(2',3'b) = 10.4$, $^3J(1',2') = 5.2$, H–C(2')); 5.42 (*ddt*, $^3J(2',3'a) = 17.3$, $^2J(3'a,3'b) = {}^4J(1',3'a) = 1.6$, H_a–C(3')); 5.29 (*ddt*, $^3J(2',3'b) = 10.4$, $^2J(3'a,3'b) = {}^4J(1',3'b) = 1.6$, H_b–C(3')); 4.54 (*ddd*, $^3J(1',2') = 5.2$, $^4J(1',3'a) = {}^4J(1',3'b) = 1.6$, 2 H–C(1')); 1.32 (*s*, $(CH_3)_3$C(1'')). ^{13}C-NMR (25 MHz, $CDCl_3$): 156.33 (*s*, C(1)); 143.48 (*s*, C(4)); 133.61 (*d*, C(2')); 126.17 (*d*, C(3),C(5)); 117.42 (*t*, C(3')); 114.24 (*d*, C(2),C(6)); 68.94 (*t*, C(1')); 34.19 (*s*, C(1'')); 31.66 (*q*, C(2'')). MS: 190 (23, $M^{+\cdot}$), 176 (14), 175 (100), 145 (17), 107 (9), 105 (12), 91 (17), 77 (9), 42 (30), 40 (17). Anal. calc. for $C_{13}H_{18}O$ (190.29): C 82.06, H 9.53; found: C 81.82, H 9.23.

*2-Allyl-4-(*tert*-butyl)phenol* (**23**)[2]. A stream of N_2/BCl_3 (*ca.* 130 mol) was bubbled through a soln. of **22** (24.5 g, 129 mmol) in chlorobenzene (1.16 l) at 10–15° during 1 h. The resulting esters of boric acid were destroyed by slow addition of MeOH (260 ml) and subsequent stirring for 1 h. Evaporation at 15 Torr afforded 23.8 g of crude product, which was distilled over a 10-cm *Vigreux* column at 125°/Torr: **23** (22.9 g, 93%) as a colorless liquid, 96.2% pure by GLC. $n_D^{20} = 1.5245$ [45] [44]. UV ($CHCl_3$): 276 (2.3), 239 (8.9). IR ($CHCl_3$): 3600*s*, 3600–3400*m*, 3010*m*, 2970*s*, 2900*m*, 2880*m*, 1640*w*, 1500*s*, 1370*m*, 1330*w*, 1270*s*, 1170*s*, 1130*s*, 1000*w*, 920*w*, 890*w*, 820*w*. ^{1}H-NMR (200 MHz, $CDCl_3$): 7.25–7.10 (*m*, H–C(3), H–C(5)); 6.78–6.72 (*m*, H–C(6)); 6.03 (*ddt*, $^3J(2',3'a) = 16.9$, $^3J(2',3'b) = 10.1$, $^3J(1',2') = 6.4$, H–C(2')); 5.19 (*ddt*, $^3J(2',3'a) = 16.9$, $^2J(3'a,3'b) = {}^4J(1',3'a) = 1.8$, H_a–C(3')); 5.17 (*ddt*, $^3J(2',3'b) = 10.1$, $^2J(3'a,3'b) = {}^4J(1',3'b) = 1.8$, H_b–C(3'));

4.88 (br. *s*, 1 OH, exchanges with D_2O); 3.41 (*ddd*, $^3J(1',2') = 6.4$, $^4J(1',3'a) = {}^4J(1',3'b) = 1.8$, 2 H–C(1')); 1.28 (*s*, $(CH_3)_3C(1'')$). ^{13}C-NMR (50,28 MHz, $CDCl_3$): 151.62 (*s*, C(1)); 143.61 (*s*, C(4)); 136.66 (*d*, C(2')); 127.25 (*d*, C(5)); 124.61 (*s*, C(2)); 124.51 (*d*, C(3)); 116.21 (*d*, C(6)); 115.28 (*t*, C(3')); 35.41 (*t*, C(1')); 34.01 (*s*, C(1'')); 31.52 (*q*, C(2'')). MS: 190 (19, $M^{+\cdot}$), 176 (14), 175 (100), 147 (10), 135 (7), 133 (7), 115 (5), 107 (11), 91 (8), 77 (5), 42 (10), 40 (7). Anal. calc. for $C_{13}H_{18}O$ (190.29): C 82.06, H 9.53; found: C 81.78, H 9.61.

*2-Allyl-4-(*tert*-butyl)phenyl Allyl Ether* (**24**)[2]. As described for **22**, **24** was prepared from **23** (22.9 g, 120 mmol). Distillation at 120°/15 Torr furnished 24.1 g (87%) of **24** as a colourless liquid (91.9% pure by GLC) [45]. $n_D^{24} = 1.5098$. UV ($CHCl_3$): 276 (2.5), 239 (17.0). IR ($CHCl_3$): 3090*w*, 3010*m*, 2970*s*, 2910*s*, 2870*m*, 1640*m*, 1610*w*, 1500*s*, 1460*m*, 1430*m*, 1365*s*, 1310*m*, 1270*s*, 1250*s*, 1140*s*, 1120*m*, 1000*s*, 920*s*, 880*w*, 810*w*. ^{1}H-NMR (400 MHz, $CDCl_3$): 7.18–7.13 (*m*, H–C(3), H–C(5)); 6.79–6.75 (*m*, H–C(6)); 6.10–5.95 (*m*, H–C(2'), 1 H–C(2'')); 5.45 (*ddt*, $^3J(2',3'a) = 17.3$, $^2J(3'a,3'b) = {}^4J(1',3'a) = 1.6$, H_a–C(3')); 5.28 (*ddt*, $^3J(2',3'b) = 10.6$, $^2J(3'a,3'b) = {}^4J(1',3'b) = 1.6$, H_b–C(3')); 5.10 (*ddt*, $^3J(2'',3''a) = 17.1$, $^2J(3''a,3''b) = {}^4J(1'',3''a) = 2.1$, H–C(3'')); 5.06 (*ddt*, $^3J(2'',3''b) = 10.0$, $^2J(3''a,3''b) = {}^4J(1'',3''b) = 2.1$, H_b–C(3'')); 4.54 (*ddd*, $^3J(1',2') = 5.0$, $^4J(1',3'a) = {}^4J(1',3'b) = 1.6$, 2 H–C(1')); 3.44 (*ddd*, $^3J(1'',2'') = 6.6$, $^4J(1'',3''a) = {}^4J(1'',3''b) = 2.1$, 2 H–C(1'')); 1.31 (*s*, $(CH_3)_3C(1''')$). ^{13}C-NMR (25.2 MHz, $CDCl_3$): 153.96 (*s*, C(1)); 143.19 (*s*, C(4)); 137.14 (*d*, C(2'')); 133.70 (*d*, C(2')); 128.14 (*s*, C(2)); 126.92 (*d*, C(3)); 123.60 (*d*, C(5)); 116.57 (*t*, C(3')); 115.12 (*t*, C(3'')); 111.16 (*d*, C(6)); 68.87 (*t*, C(1')); 34.83 (*t*, C(1'')); 34.11 (*s*, C(1''')); 31.61 (*q*, C(2''')). MS: 230 (36, $M^{+\cdot}$), 216 (18), 215 (100), 190 (10), 175 (44), 173 (14), 159 (15), 147 (21), 131 (15), 133 (15), 119 (13), 115 (14), 105 (17), 91 (19), 77 (13), 57 (44). Anal. calc. for $C_{16}H_{22}O$ (230.35): C 83.43, H 9.63; found: C 83.71, H 9.73.

*2,6-Diallyl-4-(*tert*-butyl)phenol* (**25**)[2]. As described for **23**, **25** was prepared from **24** (23.0 g, 100 mmol). The crude product (23.0 g) was chromatographed on SiO_2 (700 g, 6 × 50 cm; pentane/Et_2O 7:3) and distilled at 142°/15 Torr: 14.4 g (63%) of **25** as a slightly yellow, light-sensitive oil (97.1% pure by GLC) [45]. $n_D^{24} = 1.5222$. UV ($CHCl_3$): 281 (2.6), 239 (1.6). IR ($CHCl_3$): 3520*s*(br.), 3090*s*, 3010*m*, 2970*s*, 2910*s*, 2870*m*, 1640*m*, 1485*s*, 1430*m*, 1370*s*, 1330*w*, 1190*s*, 1120*m*, 1000*s*, 920*s*, 880*m*, 820*w*. ^{1}H-NMR (200 MHz, $CDCl_3$): 7.04 (*s*, H–C(3), C(5)); 6.05 (*ddt*, $^3J(2',3'a) = 17.1$, $^3J(2',3'b) = 10.2$, $^3J(1',2') = 6.4$, 2 H–C(2')); 5.19 (*ddt*, $^3J(2',3'a) = 17.1$, $^2J(3'a,3'b) = {}^4J(1',3'a) = 1.7$, 2 H_a–C(3')); 5.16 (*ddt*, $^3J(2',3'b) = 10.2$, $^2J(3'a,3'b) = {}^4J(1',3'b) = 1.7$, 2 H_b–C(3')); 5.08 (*s*, OH, exchanges with D_2O); 3.43 (*ddd*, $^3J(1',2') = 6.4$, $^4J(1',3'a) = {}^4J(1',3'b) = 1.7$, 4 H–C(1')); 1.31 (*s*, $(CH_3)_3C(1'')$). ^{13}C-NMR (25.2 MHz, $CDCl_3$): 150.13 (*s*, C(1)); 143.05 (*s*, C(4)); 136.72 (*d*, C(2')); 125.38 (*d*, C(3), C(5)); 124.87 (*s*, C(2), C(6)); 116.00 (*t*, C(3')); 35.64 (*t*, C(1')); 34.04 (*s*, C(1'')); 31.61 (*q*, C(2'')). MS: 230 (19, $M^{+\cdot}$), 215 (100), 174 (6), 159 (5), 145 (6), 131 (5), 129 (5), 128 (7), 115 (8), 117 (13), 91 (7), 77 (15), 57 (6), 51 (7), 42 (13), 40 (8). Anal. calc. for $C_{16}H_{22}O$ (230.35): C 83.43, H 9.63; found: C 83.18, H 9.73.

O-*[2,6-Diallyl-4-(*tert*-butyl)-1-phenyl]* N,N-*Dimethylthiocarbamate* (**27**). In analogy to [30], **25** (13.8 g, 60.0 mmol) was slowly added to a suspension of NaH (1.44 g, 60 mmol) in DMF (100 ml) under Ar at 25°. N,N-*Dimethylthiocarbamoyl chlorid* (**26**; 12.4 g, 100 mmol) was injected at 10° and the mixture stirred for 3 h at 50°. The resulting suspension was poured into H_2O (300 ml) and extracted 3 times with CH_2Cl_2. The combined org. layers were washed once with 10% KOH soln. and 3 times with sat. NaCl soln., dried (Na_2SO_4), and evaporated: 22.9 g of a yellow, crystalline product. Crystallisation from 60 ml of MeOH afforded light yellow crystals of **27** (15.0 g, 79%) 96.5% GLC-pure. M.p. 95.8–96.8°. Further crystallisation from MeOH furnished colourless needles. M.p. 97.2–97.5°. UV ($CHCl_3$): 253 (25.4). IR ($CDCl_3$): 3080*w*, 2970*s*, 2910*m*, 2870*w*, 1640*m*, 1600*w*, 1530*s*, 1480*s*, 1430*w*, 1400*s*, 1365*m*, 1290*s*, 1180*s*, 1150*s*, 1000*w*, 920*m*, 875*w*. ^{1}H-NMR (200 MHz, $CDCl_3$): 7.12 (s, H–C(3), H–C(5)); 5.97 (*ddt*, $^3J(2',3'a) = 17.7$, $^3J(2',3'b) = 9.4$, $^3J(1',2') = 6.6$, 2 H–C(2')); 5.06 (*ddt*, $^3J(2',3'a) = 17.7$, $^2J(3'a,3'b) = 2.0$, $^4J(1',3'a) = 1.3$, 2 H_a–C(3')); 5.03 (*ddt*, $^3J(2',3'b) = 9.4$, $^2J(3'a,3'b) = 2.0$, $^4J(1',3'b) = 1.3$, 2 H_b–C(3')); 3.47, 3.33 (2*s*, $(CH_3)_3N$); 3.27 (*ddd*, $^3J(1',2') = 6.6$, $^4J(1',3'a) = 1.3$, 4 H–C(1')); 1.31 (*s*, $(CH_3)_3C(1'')$). ^{13}C-NMR (25.2 MHz, $CDCl_3$): 186.26 (*s*, C=S); 148.46 (*s*, C(4)); 147.77 (*s*, C(1)); 136.40 (*d*, C(2')); 131.79 (*s*, C(2),C(6)); 125.09 (*d*, C(3),C(5)); 115.65 (*t*, C(3')); 43.24, 38.36 (2*q*, $(CH_3)_2N$); 35.16 (*t*, C(1')); 34.48 (*s*, C(1'')); 31.44 (*q*, C(2'')). MS: 317 (5, $M^{+\cdot}$), 276 (5), 245 (12), 189 (8), 157 (6), 129 (4), 128 (4), 115 (4), 88 (100), 73 (5), 72 (61), 57 (39), 42 (5), 41 (9). Anal. calc. for $C_{19}H_{27}NOS$ (317.50): C 71.88, H 8.57, N 4.41, S 10.10; found: C 71.98, H 8.40, N 4.50, S 10.29.

S-*[2,6-Diallyl-4-(*tert*-butyl)-1-phenyl]* N,N-*Dimethylthiocarbamate* (**28**). At 275–285°, **27** (1.65 g, 5.20 mmol) was heated neat in a metal bath under Ar. The reaction was complete after 1 h (TLC (SiO_2), Et_2O/pentane 3:7; R_f(**27**) 0.66, R_f(**28**) 0.32). The mixture was purified by CC on SiO_2 (80 g, 2.5 × 20 cm; Et_2O/pentane 1:9) to give light yellow crystalline **28** (1.03 g, 62%), 96.9% pure by GLC. M.p. 65–68°. Crystallisation from MeOH afforded pure **28** as colourless needles. M.p. 68.0–69.5°. UV ($CHCl_3$): 240 (14.0). IR ($CHCl_3$): 3000*w*, 2960*s*, 2870*w*, 1660*s* (C=O), 1590*w*, 1400*w*, 1365*s*, 1260*m*, 1095*s*, 1045*w*, 995*w*, 910*m*, 870*w*. ^{1}H-NMR (200 MHz, $CDCl_3$): 7.20 (*s*, H–C(3), H–C(5)); 5.98 (*ddt*, $^3J(2',3'a) = 17.2$, $^3J(2',3'b) = 10.0$, $^3J(1',2') = 6.6$, 2 H–C(2')), 5.03 (*ddt*,

^3J(2',3'a) = 17.2, ^2J(3'a,3'b) = 2.0, ^4J(1',3'a) = 1.5, 2 H_a–C(3'); 4.99 (*ddt*, ^3J(2',3'b) = 10.0, ^2J(3'a,3'b) = 2.0, ^4J(1',3'a) = 1.5, 2 H_b–C(3')); 3.59 (*ddd*, ^3J(1',2') = 6.6, ^4J(1',3'a) = ^4J(1',3'b) = 1.5, 4 H–C(1')); 3.11, 3.04 (2 br. *s*, $(CH_3)_2N$); 1.30 (*s*, $(CH_3)_3C(1'')$). ^{13}C-NMR (25.2 MHz, $CDCl_3$): 166.03 (*s*, C=O); 152.45 (*s*, C(4)); 144.61 (*s*, C(2),C(6)); 137.20 (*d*, C(2')); 124.90 (*d*, C(3),C(5)); 124.03 (*s*, C(1)); 115.44 (*t*, C(3')); 39.59 (*t*, C(1')); 36.80 (*q*, $(CH_3)_2N$); 34.57 (*s*, C(1'')); 31.11 (*q*, C(2'')). MS: 317 (4, $M^{+\cdot}$), 245 (10), 189 (9), 157 (6), 115 (4), 88 (4), 73 (4), 72 (100), 57 (49), 42 (3), 41 (9). Anal. calc. for $C_{19}H_{27}NOS$ (317.50): C 71.88, H 8.57, N 4.41; found: C 71.54, H 8.25, N 4.48, S 10.41.

S-*[(*tert*-Butyl)-2,6-bis(3-hydroxypropyl)-1-phenyl* N,N-*Dimethylthiocarbamate* (**29**). In analogy to [34], a soln. of **28** (4.00 g, 12.6 mmol) in THF (17 ml) was added within 20 min under Ar at 25° to a stirred suspension of 9-borabicyclo[3.3.1]nonane (9-BBN; 6.73 g, 88.8 mmol) in THF (20 ml). The resulting clear yellow soln. was stirred for 45 min at 25° and for further 2.5 h at 65°. Then, 20 ml of 3M NaOH were added slowly at 0° followed by 20 ml of 30% aq. H_2O_2 soln. After 15 min stirring at 25°, the H_2O phase was saturated with NaCl and extracted 3 times with THF. The combined org. layers were washed with sat. NaCl soln., dried (Na_2SO_4), and evaporated to yield an oily residue which was purified by CC on SiO_2 (300 g, 5.5 × 26 cm; $CHCl_3$/MeOH 9:1): **29** (4.23 g, 95%) as a very viscous, colourless oil, pure by TLC (SiO_2, $CHCl_3$/MeOH 9:1, R_f 0.42). The material was dried for 3 d at 0.01 Torr and became finally solid on standing for several weeks at 4°. M.p. 74–76°. UV ($CHCl_3$): 282 (0.7), 272 (0.8), 242 (5.8). IR ($CHCl_3$): 3620*m*, 3600–3200*w* (br.), 3010*m*, 2960*s*, 2880*m*, 1660*s* (C=O), 1600*w*, 1410*w*, 1370*s*, 1260*m*, 1100*s*, 1060*m*, 910*w*. ^{1}H-NMR (200 MHz, $CDCl_3$): 7.19 (*s*, H–C(3), C(5)); 3.63 (*t*, ^3J(2',3') = 6.2, 4 H–C(3')); 3.16, 3.02 (br. *s*, $(CH_3)_2N$); 2.89 (*t*, ^3J(1',2') = 7.5, 4 H–C(1')); 1.96 (*s*, 2 OH, exchange with D_2O); 1.87 (*tt*, ^3J(1',2') = 7.5, ^3J(2',3') = 6.2, 4 H–C(2')); 1.31 (s, $(CH_3)_3C(1'')$). ^{13}C-NMR (50.3 MHz, $CDCl_3$): 167.51 (*s*, C=O); 152.67 (*s*, C(4)); 146.53 (*s*, C(2), C(6)); 124.63 (*d*, C(3),C(5)); 123.72 (*s*, C(1)); 61.87 (*t*, C(3')); 37.04 (*q*, $(CH_3)_2N$); 34.49 (*s*, C(1'')); 33.56 (*t*, C(2')); 31.32 (*t*, C(1')); 31.10 (*q*, C(2'')). CI-MS: 354 (100, $[M + 1]^+$), 336 (45, $[M - H_2O]^+$), 318 (23, $[M - 2H_2O]^+$), 290 (10), 145 (9), 127 (9), 109 (25). Anal. calc. for $C_{19}H_{31}NO_3S$ (353.53): C 64.55, H 8.89, N 3.96, S 9.07; found: C 63.93, H 8.90, N 3.78, S 8.80.

S-*[2,6-Bis(3-bromopropyl)-4-(*tert*-butyl)-1-phenyl]* N,N-*Dimethylthiocarbamate* (**19**). A soln. of **29** (1.35 g, 3.82 mmol), CBr_4 (5.08 g, 15.3 mmol), and Ph_3P (4.01 g, 15.3 mmol) in Et_2O (50 ml) under Ar was stirred for 6 h at 25° in the dark [35]. Ph_3PO was than removed by filtration and washed 3 times with Et_2O. The combined Et_2O layers were filtered through cotton, evaporated, and the residue subjected to CC on SiO_2 (200 g, 5.5 × 18 cm; Et_2O) to give 1.89 g of a colourless oil which was rechromatographed on SiO_2 (150 g, 4 × 26 cm; CH_2Cl_2) to furnish **19** (1.18 g, 64%), pure by TLC (SiO_2, CH_2Cl_2, R_f 0.39). On drying at 0.01 Torr, **19** became solid. M.p. 66.5–68.0°. UV ($CHCl_3$): 281 (0.9), 272 (1.1), 250 (sh, 4.4), 241 (5.8). IR (film): 3010*m*, 2970*s*, 2870*m*, 1665*s* (C=O), 1600*m*, 1565*w*, 1480*m*, 1450*m*, 1410*m*, 1365*s*, 1260*s*, 1245*m*, 1235*m*, 1205*w*, 1095*s*, 1045*m*, 910*m*, 880*m*, 850*w*, 755*s*, 690*m*, 655*m*. ^{1}H-NMR (400 MHz, $CDCl_3$): 7.21 (*s*, H–C(3), H–C(5)); 3.42 (*t*, ^3J(2',3') = 6.5, 4 H–C(3')); 3.17, 3.01 (2 br. *s*, $(CH_3)_2N$); 2.91 (*t*, ^3J(1',2') = 7.5, 4 H–C(1')); 2.13 (*tt*, ^3J(1',2') = 7.5, ^3J(2',3') = 6.5, 4 H–C(2')); 1.31 (*s*, $(CH_3)_3C(1'')$). ^{13}C-NMR (50 MHz, $CDCl_3$): 166.62 (C=O); 152.90 (C(4)); 145.77 (C(2),C(6)); 125.55 (C(3),C(5)); 123.97 (C(1)); 37.09 $(CH_3)_2N$); 34.57 (C(1'')); 33.93, 33.80, 33.78 (C(1'), C(2'), C(3')); 31.16 (C(2'')). MS (*m/z* ≥ 25%, except $M^{+\cdot}$): 481 (6, $[M(^{81}Br^{81}Br)]^{+\cdot}$), 479 (12, $[M(^{81}Br^{79}Br)]^{+\cdot}$), 477 (5, $[M^{79}Br^{79}Br]^{+\cdot}$), 436 (32), 434 (62), 432 (28), 400 (34), 398 (31), 377 (50), 375 (100), 373 (50), 328 (30), 326 (27), 313 (81), 311 (82), 190 (30), 189 (35), 175 (35), 163 (39), 161 (58), 155 (29), 149 (30), 148 (29), 147 (50), 143 (27), 142 (29), 141 (48), 130 (29), 129 (72), 128 (87), 116 (30), 115 (80), 90 (55). Anal. calc. for $C_{19}H_{29}Br_2NOS$ (479.31): C 47.61, H 6.10, Br 33.34, N 2.92, S 6.69; found: C 47.73, H 6.20, Br 33.18, N 3.05, S 6.82.

*4-(*tert*-Butyl)-1-phenyl* N,N-*Dimethylthiocarbamate* (**31**)[2]. A soln. of *4-(*tert*-butyl)thiophenol* (**32**) (1.00 g, 6.01 mmol) and *N,N*-dimethylcarbamoyl chloride (647 mg, 6.02 mmol) in 10 ml of pyridine was stirred for 20 min at 40° under Ar. The mixture was poured into H_2O (10 ml) and extracted 3 times with CH_2Cl_2. The org. layers were than washed 3 times with H_2O and dried (Na_2SO_4) to give, after evaporation, a colourless solid. Crystallisation from MeOH afforded **31** (1.06 g, 74%) as colourless needles, pure by TLC (SiO_2, Et_2O/pentane 3:7; R_f 0.71) [46]. M.p. 71.0–72.0° UV ($CHCl_3$): 246 (10.2). IR (KBr): 3040*w*, 2960*s*, 2870*m*, 1915*w*, 1660*s* (C=O), 1600*w*, 1490*m*, 1465*m*, 1410*m*, 1400*m*, 1390*m*, 1360*s*, 1310*w*, 1265*s*, 1200*w*, 1100*s*, 1025*w*, 1015*s*, 900*m*, 830*s*, 730*m*, 690*s*, 655*s*. ^{1}H-NMR (200 MHz, $CDCl_3$): 7.42 (*s*, H–C(2), H–C(6), H–C(3), H–C(5)); 3.06 (br. *s*, $(CH_3)_2N$); 1.33 (*s*, $(CH_3)_3C(1')$). ^{13}C-NMR (50 MHz, $CDCl_3$): 167.16 (C=O); 152.19 (C(4)); 135.30 (C(2),C(6)); 125.96 (C(3),C(5)); 125.17 (C(1)); 36.78 ($(CH_3)_2N$); 34.61 (C(1')); 31.1 (C(2')). MS: 237 (7, $M^{+\cdot}$), 72 (100). Anal. calc. for $C_{13}H_{19}NOS$ (237.36): C 65.78, H 8.07, N 5.90, S 13.50; found: C 65.81, H 8.06, N 5.73, S 13.28.

*5,15-{[[4-(*tert*-Butyl)-2-(*N,N*-dimethylcarbamoyl)thio-1,3-phenylene]bis(trimethyleneoxy)]di-2,1-phenylene}-10,20-(undecamethylenedioxydi-2,1-phenylene)porphyrin* (**30**). As described for **15**, **13**/**14** (7:3; 547 mg, 0.659 mmol) was treated with **19** (379 mg, 0.791 mmol) in the presence of Cs_2CO_3 (3.22 g, 11.9 mmol). After workup, the

residue was subjected to CC on SiO_2 (45 g, 2.5 × 20 cm; CH_2Cl_2/0.75% MeOH) and **30** collected from several fractions. Rechromatography by LPLC (SiO_2, CH_2Cl_2/0.75% MeOH) afforded **30** (178 mg, 24%) still contaminated by minor impurities as evident from TLC (SiO_2, CH_2Cl_2/0.75% MeOH, R_f (**30**) = 0.46). Spectroscopically pure samples of **30** were obtained by additional chromatography on TLC (SiO_2, CH_2Cl_2/0.75% MeOH). Subsequent crystallisation from MeOH afforded microcrystalline, analy. pure **30**. M.p. > 300°. UV/VIS (toluene): 651 (2.5), 594 (4.9), 551 (6.2), 517 (15.7), 484 (3.3), 423 (331), 406 (sh, 67.4), 372 (17.8), 355 (sh, 15.7). IR (KBr): 2920*s*, 2850*m*, 1660*s* (C=O), 1595*m*, 1580*w*, 1490*m*, 1465*m*, 1445*s*, 1360*m*, 1250*s*, 1225*s*, 1185*w*, 1160*w*, 1105*m*, 1045*m*, 980*w*, 965*s*, 800*s*, 750*s*, 725*m*, 650*w*. ^{1}H-NMR (400 MHz, $CDCl_3$)[6]: 8.92, 8.80 (2 *d*, ^3J = 4.7, *AB*, 4 H–C(β) of pyrrole)); 8.58, 8.42 (2 *d*, ^3J = 4.7, *AB*, 4 H–C(β) of pyrrole); 8.53 (*dd*, ^3J(5′,6′) = 7.3, ^4J(4′,6′) = 1.7, 2 H–C(6′)); 8.13 (*dd*, ^3J(5″a,6″a) = 7.3, ^4J(4″a,6″a) = 1.7, H_a–C(6″)); 7.73 (*ddd*, ^3J(3″a,4″a) = 8.2, ^3J(4″a,5″a) = 7.4, ^4J(4″a,6″a) = 1.7, H_a–C(4″)); 7.71 (*ddd*, ^3J(3′,4′) = 8.0, ^3J(4′,5′) = 7.3, ^4J(4′,6′) = 1.7, 2 H–C(4′)); 7.57 (*ddd*, ^3J(5″b,6″b) = 8.1, ^3J(4″b,5″b) = 7.3, ^4J(3″b,5″b) = 1.7, H_b–C(5″)); 7.46 (*dd*, ^3J(4′,5′) = ^3J(5′,6′) = 7.3, 2 H–C(5′)); 7.40 (*dd*, ^3J(4″a,5″a) = 7.4, ^3J(5″a,6″a) = 7.3, H_a–C(5″)); 7.27 (*d*, ^3J(3″a,4″a) = 8.2, H_a–C(3″)); 7.13 (*d*, ^3J(5″b,6″b) = 8.1, H_b–C(6″)); 7.12 (*d*, ^3J(3′,4′) = 8.0, 2 H–C(3′)); 7.04 (*dd*, ^3J(3″b,4″b) = ^3J(4″b,5″b) = 7.3, H_b–C(4″)); 6.82 (*dd*, ^3J(3″b,4″b) = 7.3, ^4J(3″b,5″b) = 1.7, H_b–C(3″)); 6.51 (*s*, H–C(4‴), H–C(6‴)); 3.84–3.76 (*m*, 4 H–C(α″)); 3.74–3.66 (*m*, 4 H–C(α′)); 1.7 (br. *s*, CH_3N); 1.17 (*s*, $(CH_3)_3$C–C(5‴)); 0.98–0.68 (*m*, 4 H–C(β′), 4 H–C(β″), 2 H–C(γ′); 0.40–0.30 (*m*, 2 H–C(γ′)); −0.04 to −0.13 (*m*, 2 H–C(γ″)); −0.12 to −0.21 (*m*, 2 H–C(γ″)); −0.19 to −0.28 (*m*, 2 H–C(δ″)); −0.30 to −0.39 (*m*, 2 H–C(δ″)); −0.70 to −0.88 (*m*, 4 H–C(ε″), 2 H–C(μ″)); −1.3 (br. *s*, CH_3N); −2.27 (*s*, 2 NH). ^{13}C-NMR (50 MHz, $CDCl_3$): 166.43 (C=O); 160.25 (C(2′)); 159.74, 158.88 (C(2″)); 150.73 (C(5‴)); 146 (v. br., C(α) of pyrrole); 144.94 (C(1‴), C(3‴)); 135.12, 134.78 (C(6″)); 133.52 (C(6′)); 131.97 (C(1″)), 131.79 (C(1′)); 130.44 (br., C(β) of pyrrole, C(1″)); 129.72 (C(4′)); 129.61, 129.14 (C(4″)); 123.58 (C(2‴)); 122.87 (C(4‴), C(6‴)); 119.39 (C(5′), C(5″)); 119.06 (C(5″)); 116.57, 114.46 (C(*meso*″)); 115.32 (C(meso′)); 112.93, 112.34 (C(3″)); 112.41 (C(3′)); 69.05, 68.81 (C(α′), C(α″)); 34.24 $(CH_3)_3C$); 31.30 ($CH_3)_3$C); 30.97, 30.86 ($(CH_3)_2$N); 30.44, 29.30, 28,61, 28.53, 27.90, 27.74, 27.69, 27.50, 27.05, 25.57, 25.56 (C(β′), C(β″) (2 signals), C(γ′), C(γ″) (2 signals), C(δ″) (2 signals), C(ε″) (2 signals), C (μ″)). MS: 1150 (18), 1149 (42), 1148 (82), 1147 (100, $M^{+\cdot}$), 1146 (9), 1079 (10), 1078 (25), 1077 (53), 1076 (87, $[M - (C(O)N(CH_3) + H]^+$), 1075 (75), 1074 (12), 1073 (8), 832 (9), 831 (12, $[M - ((CH_2)_3C_6H_2(SC(O)N(CH_3)_2)\,C_4H_9(CH_2)_3) + H_3]^+$), 830 (8), 829 (9), 677 (7, $[M - ((CH_2)_6C_6H_2$ $(SC(O)N(CH_3)_2)C_4H_9\,(CH_2)_{11}) + H_3]^+$), 675 (6).

*5,15-{[[4-(*tert*-Butyl)-2-mercapto-1,3-phenylene]bis(trimethyleneoxy)]di-2,1-phenylene}-10,20-(undecamethylenedioxyl-2,1-phenylene)porphyrin* (**33**). A 1.8M solution of K in MeOH (13 ml) was injected into a soln.[7]) of **30** (102 mg, 0.089 mmol) in dioxan (13 ml) and the mixture refluxed under a constant stream of Ar. After 1 h, the transformation was complete according to TLC (SiO_2, CH_2Cl_2/0.75% MeOH; R_f (**33**) = 0.77; R_f (**30**) = 0.46), and the soln. poured into sat. NH_4Cl soln. Extraction with toluene, washing of the combined org. layers with H_2O, drying (Na_2SO_4), and evaporation furnished a solid residue (103 mg). The crude product was purified by CC on SiO_2 (55 g, 2.5 × 24 cm, degassed with Ar; toluene) to yield pure **33** (48.0 mg, 50%) from the the first purple band. Crystallisation from MeOH/CH_2Cl_2 gave an anal. pure, microcrystalline sample. M.p. 220–222°. UV/VIS (toluene): 649 (2.2), 593 (5.2), 550 (5.7), 516 (16.9), 484 (3.2), 422 (366), 405 (sh, 71.4), 372 (20.5), 354 (sh, 17.5). IR (KBr): 2920*s*, 2860*s*, 1600*m*, 1580*w*, 1490*m*, 1465*m*, 1445*s*, 1350*w*, 1270*w*, 1250*s*, 1230*s*, 1185*w*, 1160*w*, 1110*m*, 1045*m*, 995*w*, 980*w*, 965*m*, 800*s*, 750*s*, 725*s*, 650*w*. ^{1}H-NMR (400 MHz, $CDCl_3$): 8.75, 8.72 (2 *d*, ^3J = 4.7, *AB*, 8 H–C(β) of pyrrole); 8.55 (*dd*, ^3J(5′,6′) = 7.4, ^4J(4′,6′) = 1.7, 2 H–C(6′)); 8.10 (*dd*, ^3J(5″,6″) = 7.4, ^4J(4″,6″) = 1.7, 2 H–C(6″)); 7.75 (*ddd*, ^3J(3′,4′) = 8.2, ^3J(4′,5′) = 7.6, ^4J(4′,6′) = 1.7, 2 H–C(4′)); 7.69 (*ddd*, ^3J(3″,4″) = 8.2, ^3J(4″,5″) = 7.6, ^4J(4″,6″) = 1.7, 2 H–C(4″) = 1.7, 2 H–C(4″)); 7.50 (*ddd*, ^3J(4′,5′) = 7.6, ^3J(5′,6′) = 7.4, ^4J(3′,5′) = 0.9, 2 H–C(5′)); 7.32 (*ddd*, ^3J(4″,5″) = 7.6, ^3J(5″,6″) = 7.4, ^4J(3″,5″) = 0.9, 2 H–C(5″)); 7.24 (*dd*, ^3J(3″,4″) = 8.2, ^4J(3″,5″) = 0.9, 2 H–C(3″)); 7.16 (*dd*, ^3J(3′,4′) = 8.2, ^4J(3′,5′) = 0.9, 2 H–C(3′)); 6.26 (*s*, H–C(4‴), H–C(6‴)); 3.79 (*t*, ^3J = 5.3, 4 H–C(α″)); 3.68 (*t*, ^3J = 5.1, 4 H–C(α′)); 0.92 (*s*, $(CH_3)_3$C); 0.84–0.76 (*m*, 4 H–C(β′), 4 H–C(β″)); 0.68–0.59 (*m*, 4 H–C(γ′)); −0.02 to −0.11 (*m*, 4 H–C(γ″)); −0.18 to −0.27 (*m*, 4 H–C(δ″)); −0.62 to −0.77 (*m*, 4 H–C(ε″), 2 H–C(μ″)); −2.39 (*s*, 2 NH); −2.48 (*s*, SH). ^{13}C-NMR (50 MHz, $CDCl_3$): 159.86, 159.36 (C(2′), C(2″)). 146.43 (C(4″)); 146 (v. br., C(α) of pyrrole); 138.15 (C(1‴), C(3‴)); 135.59, 133.36 (C(6′), C(6″)); 132.25, 131.89 (C(1′), C(1″)); 130.57, 130.21 (br., C(β) of pyrrole); 129.57, 129.37 (C(4′), C(4″)); 126.64 (C(1″)); 122.92 (C(4‴), C(6‴)); 119.56, 119.30 (C(5′), C(5″)); 115.71, 114.77 (C(*meso*′), C(*meso*″)); 112.63, 112.28 (C(3′), C(3″)); 69.01, 68.39 (C(α′), C(α″)); 33.70 $(CH_3)_3C$); 31.02 ($CH_3)_3$C); 30.95, 29.09, 28.58, 27.81, 27.67, 25.57 (C(β′), C(β″), C(γ′), C(γ″), C(δ″), C(ε″)); 27.14 (C(μ″)). MS ($m/z \geq 8\%$, except $[M - S]^+$):

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[6]) The protons of the diastereotopic *meso*-aryl groups, connected by the alkane bridge, are labelled a and b.

[7]) All solvents degassed.

1131 (8), 1130 (10, [^{56}Fe-M]$^+$, impurity), 1129 (8), 1080 (8), 1079 (20), 1078 (45), 1077 (78), 1076 (100, $M^{+\cdot}$), 1075 (17), 1074 (10), 1063 (8), 1062 (13), 1061 (16, $[M - CH_3]^+$), 1044 (5, $[M - S]^+$), 1020 (8), 1019 (10, $[M - (CH_3)_3C]^+$), 832 (8), 831 (13, $[M - (CH_2)_6C_6H_2(SH)C_4H_9 + H_3]^+$).

*β-Bromo[5,15-{[[4-(*tert*-butyl)-2-mercapto-1,3-phenylene]bis(trimethyleneoxy)]di-2,1-phenylene}-10,20-(undecamethylenedioxydi-2,1-phenylene)porphyrinato]iron (III).* (**34**). $FeBr_2$ (40 mg, 0.19 mmol) was added to a refluxing soln. of **33** (15 mg, 0.014 mmol) in THF/benzene 1:1 (5 ml) containing 30 mg of 2,6-dimethylpyridine. According to TLC (SiO_2, toluene; R_f (**33**) 0.63 (purple spot), R_f (**35**) 0.56 (orange spot), R_f (**34**) 0.29 (brown spot)), after 15 min reflux, **33** was converted mainly into **34**, only small amounts of **35** were visible. The solvent was removed at 0.01 Torr and the resulting solid subjected to CC on SiO_2 (6.0 g, 1.3 × 9 cm; toluene). From the slowly moving dark-brown band, **34** was isolated nearly quantitatively as a brown microcrystalline powder. UV/VIS (toluene): 673 (4%), 568 (6%), 513 (13%), 412 (100%), 330 (29%). MS: 1133 (10), 1132 (30), 1131 (65), 1130 (100, $[M - Br]^+$), 1129 (80), 1128 (25), 1127 (16), 1126 (11), 1099 (10), 1098 (11, $[M - (Br,S)]^+$),1097 (5), 1096 (6), 1074 (7), 1073 (11), 1072 (15, $[M - (Br,(C_4H_{10}))]^+$), 886 (7), 885 (15), 884 (15, $[M - (Br,(CH_2)_6C_6H_2(SH)C_4H_9) + H_2]^+$), 883 (5), 882 (6).

*[5,15-{[[4-(*tert*-Butyl)-2-mercapto-1,3-phenylene]bis(trimethyleneoxy)]di-2,1-phenylene}-10,20-(undecamethylenedioxydi-2,1-phenylene)porphyrinato]iron (II)* (**35**). To a soln. of **34** (8.0 mg) in toluene (1.0 ml), 1.0 ml of 0.1M $Na_2S_2O_4$ was added. A permanent CO atmosphere was established by septum injection of CO into the H_2O-layer. The two-phase system was vigorously stirred at 25° in the dark leading, after 48 h, to **35**/**34** *ca.* 2:1, as judged by TLC (SiO_2, toluene). Since this ratio did not change on prolonged reaction time, the toluene layer was separated in the glove-box, filtered through cotton and subjected to CC on SiO_2 (5.0 g, 1.3 × 8 cm) with toluene. The product was isolated from the fast-moving orange band and in part directly transferred to a septum-equipped UV cell. To obtain ^{1}H-NMR spectra the toluene soln. containing **35** was evaporated at 0.01 Torr and the resulting purple residue dissolved in (D_8)toluene under N_2. **35**: UV/VIS (toluene): 541 (17%), 423 (100%), 332 (17%). ^{1}H-NMR (400 MHz, (D_8)toluene): 15.82 (*d*, $^3J(5',6') \approx 5$, 2 H–C(6')); 14.76 (*d*, $^3J(5'',6'') \approx 5$, 2 H–C(6'')); 9.71 (*dd*, $^3J(4',5') \approx 8$, $^3J(5',6') \approx 5$, 2 H–C(5')); 9.69 (*dd*, $^3J(3'',4'') \approx {}^3J(4'',5'') \approx 8$, 2 H–C(4'')); 9.58 (*dd*, $^3J(3',4') \approx {}^3J(4',5') \approx 8$, 2 H–C(4')); 9.27 (*dd*, $^3J(4'',5'') \approx 8$, $^3J(5'',6'') \approx 5$, 2 H–C(5'')); 8.44 (*d*, $^3J(3'',4'') \approx 8$, 2 H–C(3'')); 7.99 (*d*, $^3J(3',4') \approx 8$, 2 H–C(3')); 3.55 (*s*, 4 H–C(α'')); 3.15 (*s*, 4 H–C(α')); 0.30 (*s*, H–C(4'''), H–C(6''')); 0.27 (*s*, 4 H–C(β) of pyrrole); –0.98 (*s*, $(CH_3)_3C$–C(5''')); –1.85 (*s*, 4 H–C(γ')); –3.17 (*s*, 4 H–C(β) of pyrrole); –3.36 (*s*, 4 H–C(β'')); –5.85 (*s*, 4 H–C(γ'')); –7.39 (*s*, 4 H–C(β')); –9.64 (*s*, 4 H–C(δ'')); –12.92 (*s*, 4 H–C(ε'')); –16.52 (*s*, 4 H–C(μ'')); –75.90 (*s*, SH).

*[5,15-{[[4-(*tert*-Butyl)-2-sulfido-1,3-phenylene]bis(trimethyleneoxy)]di-2,1-phenylene}-10,20-(undecamethylenedioxydi-2,1-phenylene)porphyrinato*-N,N',N'',N''',S]*iron(II)* (**6**) *and [5,15-{[[4-(*tert*-Butyl)-2-sulfido-1,3-phenylene]bis(trimethyleneoxy)]di-2,1-phenylene}-10,20-(undecamethylenedioxydi-2,1-phenylene)porphyrinato*-N,N',N'',S]*-β-(carbonyl)iron(II)* (**36**). Another part of the toluene soln. of **35** obtained by CC (see above) was injected *via* septum into a UV cell containing an excess of both KH and [18]crown-6 in toluene. Anion formation was observed by color change from red-orange to green-brown. UV/VIS (**6**, toluene): 624, 450 (sh), 425, 300.

When CO was bubbled through the soln. of **6** for 15 min at 25°, **36** was produced quantitatively exhibiting a UV/VIS with a split *Soret* band. CO binding was reversible as shown by repetitive gas exchange Ar *vs.* CO. UV/VIS (**36**, toluene): 615 (5%), 555 (8%), 457 (78%), 403 (100%), 300 (49%).

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