The Reaction of Porphyrins with Organolithium Reagents

Mathias O. Senge,* Werner W. Kalisch, and Ines Bischoff[a]

Abstract: Porphyrins react readily with organolithium reagents, preferentially in the *meso* positions. The overall reaction is a nucleophilic substitution and proceeds via initial reaction of the organic nucleophile with a *meso* carbon yielding an anionic species which is hydrolyzed to a porphodimethene (5,15-dihydroporphyrin), formally constituting an addition reaction to two C_m positions. Subsequent oxidation with 2,3-dichloro-5,6-dicyano-1,4-benzoquinone (DDQ) yields *meso*-substituted porphyrins. The reaction is highly versatile as it is accomplished in high, often quantitative yields with various alkyl or aryl lithium reagents. In addition, LiR can be used for reaction with a variety of metal complexes (best with Ni^{II}, but also with Zn^{II}, Cu^{II}, and Co^{II}) and most useful with free base porphyrins. Similarly beneficial this reaction can be used in sequence for the introduction of 1, 2, 3, or 4 (different) *meso* substituents giving for the first time an entry into any desired *meso*-substituted porphyrin. If *meso*-substituted porphyrins are used, reaction with LiR can be used for either the preparation of phlorins (already known reaction), porphodimethenes (5,15-dihydroporphyrins, including those with exocyclic double bonds, for example, $5^1,5^2$-didehydroporphyrins) or chlorins (2,3-dihydroporphyrins) depending on the substituent type in the reactant porphyrins. Thus, this reaction presents a generally applicable method for the facile and versatile functionalization of porphyrins.

Keywords: alkylations · C–C coupling · lithium · nucleophilic aromatic substitutions · porphyrinoids

Introduction

Porphyrins have been the focus of intense chemical studies for almost a century beginning with the comprehensive studies of Willstätter[1] and Fischer.[2] Since then a considerable body of chemical knowledge has been accumulated.[3, 4] This is not only a result of their biological functions, which can be investigated with modern instruments in greater detail, but also of their relevance for understanding basic physicochemical processes like electron and exciton transfer. In addition, tetrapyrroles in general have potential technical use in the area of solar energy conversion,[5] catalysis,[6] nonlinear optics,[7] and an increasing number of medicinal applications,[8] including their use as photosensibilisators, fluorescence markers, and antitumor (PDT), or antiviral (PVT) agents, are being reported.

Despite their importance, the development of novel synthetic methods for tetrapyrroles has not been in step with the demand for more complex porphyrin systems coming from the applied and biological area. Indeed, several white specks remain on the porphyrin synthesis and modification map. One such case involves the lack of methods for the facile modification of preformed porphyrins. As symmetric porphyrins like 5,10,15,20-tetraphenylporphyrin {H_2(TPP) **1a**}[9a] or 2,3,7,8,12,13,17,18-octaethylporphyrin {H_2(OEP) **2a**}[9b] are easily prepared in large amounts, a subsequent modification of these compounds to more complex, asymmetrically functionalized porphyrins would be highly beneficial. A total synthesis of an OEP derivative with one additional *meso* substituent or a TPP derivative with an additional β substituent, although possible, is often impractical, especially when the desired target compound contains more than two different types of *meso*- and β substituents. Existing methods for such synthetic strategies, which are in high demand due to the above-described developments, require highly involved pyrrole and dipyrrin chemistry, followed by appropriate [2+2]- or [3+1]-condensation reactions or cyclizations.[10] Ideally, syntheses of complex porphyrins should involve easily available reagents, proceed with both high regiospecifity and yield and preferably involve reactions that, once established in a laboratory, can easily be applied to various educts and used for the introduction of highly divergent residues.

Unfortunately, porphyrins have proven to be very resilient towards many reactions that on paper should proceed quite easily, for example, Friedel–Crafts or Grignard reactions.[11] Several electrophilic substitution reactions[12] have been described over the years,[11] including *meso* methylation of Pd^{II}(OEP),[13a] reaction of porphyrins with carbenes,[13b] rearrangements of *N*-substituted porphyrins,[14a] reductive pro-

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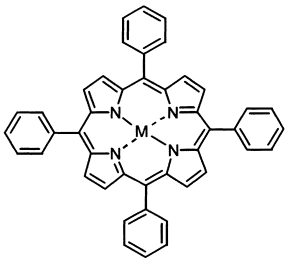
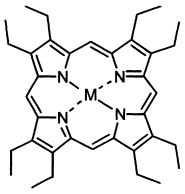


1

	M
1a	2H
1b	Ni
1c	Zn



2

	M
2a	2H
2b	Ni
2c	Zn
2d	Cu
2e	Co
2f	FeCl

tonation,[14b] and Buchler's reductive methylation.[15] Of the older reactions, the most widely used reaction is the Vilsmeier formylation which continues to be a convenient entry reaction into many other porphyrin derivatives.[16] Similarly, nitration,[17a–c] nitrene,[17d] and thiocyanation[17e] reactions have been described.[18] Of greater importance is the use of halogenation reactions,[18] notably chlorination and bromination in both the *meso*- and β positions.[6] Halogenated porphyrins are of considerable importance in catalytic applications[6] and have been used in recent years as entry points for modern C–C coupling reactions,[19] for example, Heck-[19a] and Suzuki[19b] reactions.

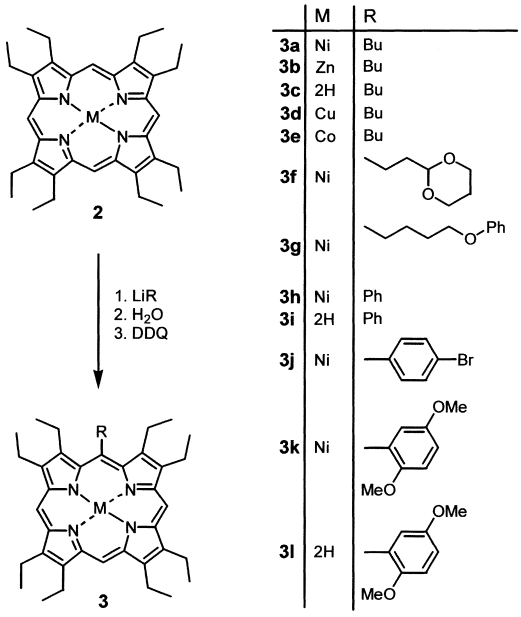
Similarly, only few examples for nucleophilic addition or substitution reactions have been described for porphyrins.[13] While porphyrins are easily reduced by electrons to the phlorins or chlorins,[20] their reactivity towards nucleophiles has only been studied rather randomly. For example, Zn^{II}(OEP) π-cation radicals and π dications,[21a] or Fe^{III}(TPP) π-cation radicals[21b] have been shown to react with nucleophiles, and several examples for use of activated porphyrins in S_N reactions have been given. Activation can be achieved either via electron-withdrawing substituents (e.g., NO_2,[17b, 22] formyl,[23]) appropriate central metals (Rh or Au),[24] or steric effects.[25, 26] In practical terms, with the exception of the alkyne-substituted porphyrins,[19d] synthetically useful is only the reaction of *meso*-brominated metalloporphyrins with organotin or organozinc reagents. For example, 5,15-dibromo-10,20-diarylporphyrins could be converted in almost quantitative yield to the 5,15-disubstituted porphyrins.[27] The reactions mentioned, either require modification of the porphyrin, are limited with regard to the type and number of substituents that can be introduced or proceed under irreversible formation of non-aromatic systems or often give only low yields.

As to date no general method exists for the direct *meso* substitution of unactivated porphyrins with alkyl or aryl residues or for the introduction of more than two *meso* substituents we have undertaken a comprehensive investigation of the reactivity of the porphyrin system towards organometallic reagents. As will be shown below, organolithium reagents present a class of reagents that fulfill all the criteria listed above and can be used to introduce, often quantitatively, almost any desired residue into the porphyrin.[28]

Results and Discussion

Reaction of LiR with 2,3,7,8,12,13,17,18-octaalkylporphyrins: Initially, we attempted the preparation of Grignard compounds starting with the 5-halogeno-2,3,7,8,12,13,17,18-octaethylporphyrins,[29] but never observed any change in the starting material. As organolithium compounds are more reactive we then attempted an halogeno-metal exchange. Reaction of (5-bromo-2,3,7,8,12,13,17,18-octaethylporphyrinato)nickel(II)[30] with *n*-butyl lithium (BuLi) in dry THF resulted in the formation of several very apolar, lightly colored products. Addition of benzaldehyde, to trap a putative organolithium porphyrin, did not change the reaction products. UV/Vis spectroscopy of the reaction mixture indicated the presence of a porphodimethene (λ_{max} in $CH_2Cl_2 = 446$ and 554 nm). For work up the reaction mixture was hydrolyzed with water and filtered through neutral alumina, which retained several polar, blue fractions. The filtrate consisted mainly of an intensively red colored fraction, with absorption maxima indicative of a porphyrin (λ_{max} in $CH_2Cl_2 = 414$ and 580 nm). Thin-layer chromatography showed this fraction to consist of two individual compounds, which could not be separated by chromatography.[31]

For more detailed studies we then performed similar reactions with Ni^{II}(OEP) **2b** treating it with various amounts of BuLi. Utilization of about four equivalents of BuLi with respect to the porphyrin resulted in formation of a lightly yellow colored solution which, upon contact with atmospheric oxygen, immediately turned brightly red (λ_{max} in $CH_2Cl_2 = 410$ and 572 nm). Spectroscopic analysis revealed the product to be the monobutylated porphyrin (5-butyl-2,3,7,8,12,13,17,18-octaethylporphyrinato)nickel(II) (**3a**). Hydrolysis of the reaction mixture at low temperatures followed by subsequent addition of an excess of DDQ resulted in complete oxidation of the intermediate to the porphyrin giving **3a** in quantitative yield (Scheme 1). Use of a larger excess of BuLi resulted in increased yields of several polar, blue products, presumably ring-opened tetrapyrroles.



Scheme 1. *meso* Monofunctionalization of (metallo)octaethylporphyrins.

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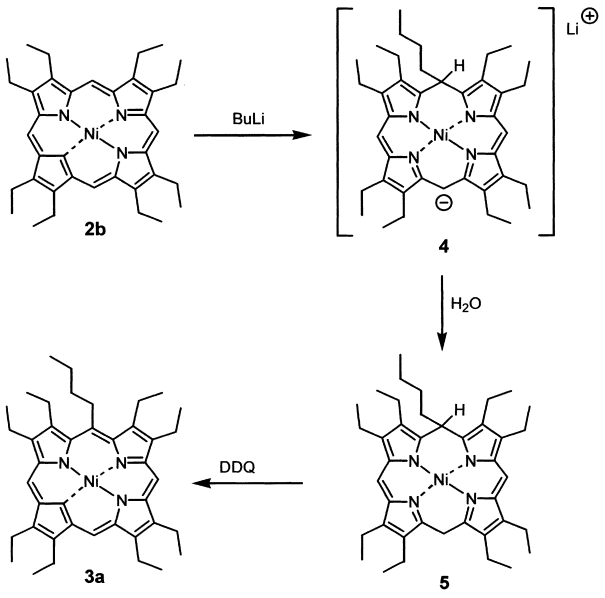
On the basis of these observations we surmised the following mechanism. First, reaction of **2b** with BuLi proceeds via addition of BuLi at two *meso* positions, giving a Meisenheimer-type complex **4** (a phlorin in porphyrin terminology) that is hydrolyzed by water to the porphodimethene **5** which in turn is oxidized to the porphyrin **3a** (Scheme 2). Thus, formally, BuLi reacts under nucleophilic substitution with Ni^{II}(OEP), presumably via an addition–oxidation mechanism (Scheme 2) akin to the Ziegler reaction.[32]



Scheme 2. Putative mechanism for the reaction of Ni^{II}(OEP) with BuLi.

In order to test the general applicability we first investigated the use of different metal complexes of OEP. The Zn^{II}, Cu^{II}, Co^{II}, and $Fe^{III}Cl$ complexes of OEP (**2c–f**) were prepared and treated with BuLi under the conditions described for Ni^{II}(OEP). Zn^{II}(OEP) **2c** gave the monobutylated product **3b** in 40% yield, however, the reaction with Zn^{II} complex always proceeded under almost complete demetallation to the corresponding free base **3c**. Cu^{II}(OEP) **2d** gave **3d** in 75% yield, while Co^{II}(OEP) **2e** was converted into **3e** in 40% yield. Use of Fe^{III}(OEP)Cl **2f** resulted only in the observation of various degradation products, no butylation of the porphyrin was observed. Generally, most metal complexes are suitable reactants for this reaction although yields were lower compared to Ni^{II}(OEP). Use of metal complexes like Zn^{II}(OEP) offers the advantage of higher solubility compared to **2b**, while reaction with Cu^{II}(OEP), despite the satisfactory yield, suffers from the low solubility of the starting material. Thus, Ni^{II} complexes were used for most other transformations.[33]

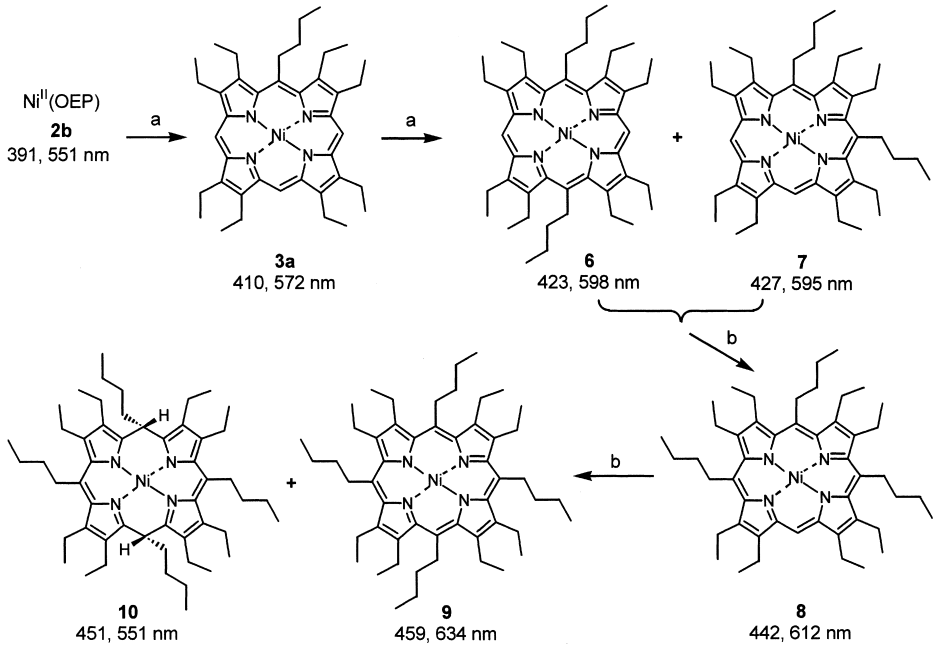
The ease of the reaction with BuLi suggested that a wide variety of alkyl lithium reagents might be applicable to the functionalization of porphyrins. Indeed, any alkyl or aryl lithium compound tested gave at least satisfactory if not excellent yields of *meso* substitution. For example, **2b** was treated with 2-(1,2-dioxane-2-yl)ethyl lithium to the protected aldehyde **3f** in 70% yield. After deprotection, this compound can be used for a variety of further modification reactions.[34] In a similar manner, introduction of protected alcohol functionalities is possible. For example, the ether **3g** was prepared in 60% yield using 4-phenoxybutyl lithium. The lithium reagents were prepared from the corresponding halogeno derivatives with di-*tert*-butylbiphenyllithium[35] and used immediately for reaction with Ni^{II}(OEP) (5–10 equiv).

Similar to the versatility of alkyl lithium reagents for the modification of porphyrins aryl lithium reagents could be used with ease. Treatment of **2b** with phenyl lithium gave the *meso*-phenylated porphyrin **3h** in 65% yield. Aryl lithium reagents gave *meso*-functionalized porphyrins amenable for further transformations. For example, the *p*-bromophenyl substituted porphyrin **3j**, suitable for a variety of further organometallic coupling reactions, was obtained in 40% yield using *p*-bromophenyllithium.[36] Use of 2,5-dimethoxyphenyllithium[37] gave the porphyrin **3k**, formally a protected *p*-quinone, suitable starting materials for entry into donor–acceptor complexes.

As shown, one *meso* substituent can be introduced into the porphyrin macrocycle in high yield, a reaction applicable to a wide variety of substrates. Thus, the question arose whether such a reaction can be repeated with the same starting porphyrin, that is, if introduction of 2-, 3-, or 4-*meso* substituents is possible. Potentially, such a sequence would allow a novel entry into dodecasubstituted nonplanar porphyrins. Thus, the monobutylated porphyrin **3a** was again treated with BuLi, the intermediate hydrolyzed with water, and oxidized with DDQ. Two different reaction products were observed, which were identified as the two regioisomers **6** and **7**, that is the Ni^{II} porphyrins with either 5,15-or 5,10-disubstitution pattern. Intriguingly, the "*cis*" (5,10)-dibutylated product **7** was obtained in 70% yield compared with 15% for the "*trans*" (5,15)-disubstituted porphyrin **6**. This preference for attack in the neighboring *meso* position (over the statistical ratio of 2:1) appears to be a general phenomenon and has been observed by us for a variety of lithium reagents.

Tri- and tetrabutylated porphyrins are accessible by this method, as well. Reaction of either **6** or **7**, or the regioisomeric mixture gave the 5,10,15-tributyl porphyrin **8**, again in quantitative yields. Use of **8** for another substitution reaction with BuLi yields the tetra-*meso* substituted porphyrin **9** in 50% yield (see Scheme 3). The remainder of the starting material was converted to the porphodimethene **10** (see below). The porphyrin **9** is a highly symmetric compound. This is evidenced in the ^{13}C-NMR spectrum that shows six aliphatic signals between $\delta = 10$ and 40; the C_m carbon atoms show a signal at $\delta = 116.59$, while the remaining 16 carbon atoms of the aromatic ring systems give two signals at $\delta =$ 135.85 and 146.48, respectively. Technically, the reaction of *meso*-butylated porphyrins is easier than that of for example **2b** as the solubility increases with the introduction of more and more alkyl chains. As expected, the polarity decreases drastically with the number of butyl chains; compound **9** is almost apolar, soluble only in hexane and purification requires neutral alumina and elution with neat hexane.

This sequence for four subsequent addition–oxidation cycles allows, for the first time, a synthesis of sterically hindered dodecaalkylporphyrins. Sterically strained porphyr-

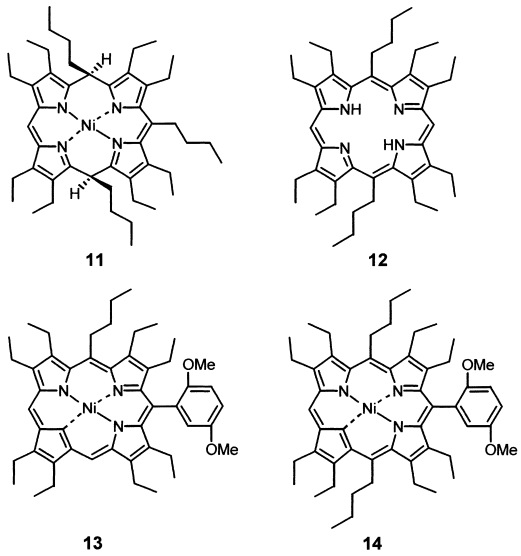


Scheme 3. Successive *meso* butylation of Ni^{II}(OEP). a) 1) BuLi, THF, $-80\,^{\circ}C$, 2) H_2O, 3) DDQ; b) 1) BuLi, THF, $-100\,^{\circ}C$, 2) H_2O, 3) DDQ. Numbers underneath formulas give main absorption maxima in CH_2Cl_2.

ins have become of prime interest in the last decade, as macrocycle conformational effects have been shown to be involved in the control of cofactor properties in intact pigment–protein complexes.[18, 38] Indeed, the majority of tetrapyrrole cofactors in vivo exhibits more or less distorted macrocycle conformations.[18, 38b,c] So-called highly substituted porphyrins[38] have found wide applications in the study of the conformational control of physicochemical properties and wide-ranging studies have been presented on nonplanar porphyrins.[38a] While several different distortion modes are possible for porphyrins, the two most widely found types of nonplanar porphyrins are macrocycles with either saddle-type or ruffled distortion modes.[38e] In the case of model compounds, the former is easily accessible by preparation of for example 5,10,15,20-tetraaryl-2,3,7,8,12,13,17,18-octaalkyl/arylporphyrins.[39] Ruffled macrocycles have been observed as the result of metal effects,[38e] and for porphyrins with bulky *meso*-alkyl substituents.[26, 40]

In this context, the synthesis of dodecasubstituted porphyrins with *meso*-alkyl substituents is of high interest, as such compounds should exhibit nonplanar macrocycles with an extreme degree of ruffling. Earlier attempts to prepare such porphyrins by standard condensation methods, that is, mixing of 3,4-disubstituted pyrroles with an alkyl aldehyde under acid catalysis, failed for sterically hindered systems.[39a] The only porphyrins accessible through this route were porphyrins involving β-cyclopentenyl rings, where the β-CH_2 groups were effectively removed from steric interactions with the *meso*-alkyl substituents due to the ring constraints.[41] A typical example involved the synthesis of (tetracyclopenta[*b*,*g*,*l*,*q*]-5,10,15,20-tetrapentylporphyrinato)nickel(II).[39a] In contrast, the attempted synthesis of tetracyclohexa[*b*,*g*,*l*,*q*]-5,10,15,20-tetraethylporphyrin yielded, after oxidation with DDQ, only the porphodimethene tetracyclohexa[*b*,*g*,*l*,*q*]-5,10,5,20-tetraethyl-5,15-dihydroporphyrin,[43] which resisted any oxidation attempts to the desired porphyrin. This problem has now been overcome with the present methodology.

In addition, the present study gives some indication on the problem involved with the oxidation resistance of sterically hindered porphodimethenes. As mentioned above, reaction of the highly nonplanar porphyrin **8** with BuLi gave the porphyrin **9** in only 50% yield, while all other reactions involving BuLi proceeded almost quantitatively to the desired porphyrins. Most of the remaining starting material was converted into the porphodimethene **10** that showed *syn*-axial orientation of the two *meso*-hydrogen atoms. This tetrapyrrole was stable against oxidants such as air, DDQ, Br_2, or *p*-chloranil, even using elevated reaction temperatures. The configuration at the sp^3-hybridized *meso* carbon atoms was unambiguously determined by single crystal X-ray crystallography (see below). As porphodimethenes of the general constitution **10** are oxidizable to the porphyrin **9**—otherwise no formation of the porphyrin would have been possible—we surmise that the specific *syn*-axial orientation of the *meso*-hydrogen atoms constitutes a configuration in which removal of the hydrogen atoms is rather difficult.[44]



Further evidence for this was obtained from the observation that brown side products (such as **10**) were frequently observed during the synthesis of porphyrins **6**–**9** when the reaction temperature was allowed to rise above $-80\,^{\circ}C$. For example, the conversion of **8** to the green porphyrin **9** is quantitative only at temperatures below $-80/-100\,^{\circ}C$. At

0947-6539/00/0615-2724 $ 17.50+.50/0 *Chem. Eur. J.* **2000**, *6*, No. 15

higher reaction temperatures the formation of a brown product, the porphodimethene **11**, was observed. At temperatures above $-30\,^{\circ}C$, formation of this product became quantitative and no porphyrin formation was observed. Again, this porphodimethene was resistant to any of the usual oxidants employed in porphyrin chemistry. A crystal structure analysis (see Figure 6) showed the same *syn*-axial configuration of the *meso*-hydrogen atoms as in any of the other nonoxidizable porphodimethenes. Presumably, thermodynamic control of the initial substitution reaction locks the porphodimethene into a configuration that is more difficult to oxidize than the one (probably *anti*-configurated) that is the normal intermediate of the porphyrin formation described here. In addition, the observation of the formation of porphodimethenes gives some indication for the validity of the mechanism for this reaction suggested above inasmuch that a porphodimethene is the product of the initial reaction (formally an addition step) in the sequence leading to substituted porphyrins described here.

The formation of different configuration isomers for 5,5′,15,15′-substituted decaalkylporphyrins has already been described by Buchler in his elegant studies on the reductive alkylation of Zn^{II}(OEP).[15] Notably, crystal structures of his stable porphodimethenes showed the same *syn*-axial orientation of the *meso*-alkyl groups as described here for **10**.[15b–d]

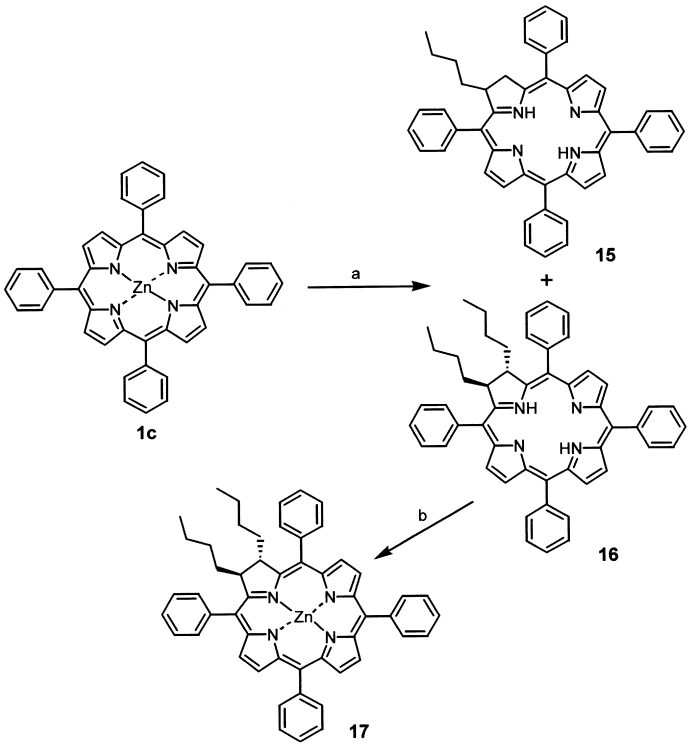
As the use of novel porphyrins in applications such as catalysis or modeling of natural electron transfer processes requires the preparation of metal complexes other than those normally employed in synthetic projects, an entry into the corresponding free bases of the porphyrins with novel substituent pattern needed to be found. Initially, we attempted demetalation using standard methodologies, for example with sulfuric acid. This method works well for unsubstituted porphyrins. For example, **3a** was demetallated in 80% yield to **3c**, **3h** in 90% yield to **3i** and **3k** to **3l** in 90% yield. Upon going to decasubstituted porphyrins the situation becomes more problematic. The symmetric porphyrin **6** was demetallated to **12** in 80% yield. In contrast, while demetallation of **7** and **8** gave the desired free bases, these were very unstable and during work up degraded to brown-blue products. Thus, the more sterically hindered (and nonplanar) the *meso* alkylporphyrins are, the more difficult the formation of the free bases becomes. The reason for this can be found in the very high reactivity of strongly ruffled alkylporphyrins towards nucleophiles, which readily react with solvate molecules at the substituted *meso* positions under disruption of the aromatic system and formation of porphodimethenes similar to those described above.[26]

With these results in mind we attempted the direct reaction of free base porphyrins with LiR. Surprisingly, the free base **2a** readily treated with BuLi in 50% yield under formation of the *meso*-butylated porphyrin **3c**. In a similar manner, reaction of **2a** with PhLi gave **3i** in quantitative yield, and reaction with 2,5-dimethoxyphenyllithium gave **3l** in 27% yield. Presumably, reaction with the free bases proceeds by initial formation of lithiated porphyrins [e.g. Li_2(OEP] as described by Arnold.[45] Thus, the LiR reagents are equally versatile for the direct substitution of free base porphyrins and metalloporphyrins.[46]

As indicated by the possibility of introducing up to four *meso* substituents through this reaction, porphyrins with mixed *meso*-substituent pattern can easily be prepared. For example, **3a** and **7** could be converted in 50% yield to the deca- and undecasubstituted porphyrins **13** and **14**, respectively. Thus, the methodology reported here, is applicable for the synthesis of basically any desired *meso*-substituted porphyrin. Detailed studies on porphyrins with mixed substituent pattern and suitable synthetic strategies will be reported elsewhere.[46]

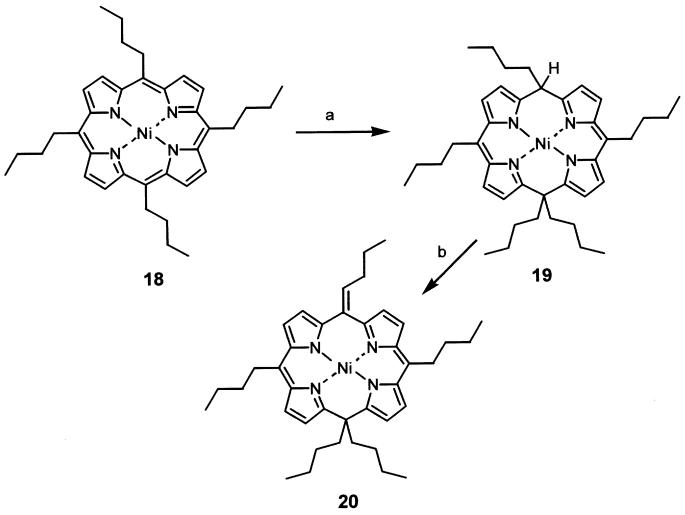
Reaction of LiR with 5,10,15,20-tetraarylporphyrins: In order to investigate the mechanism of nucleophilic additions in *meso* position in more detail the reaction of LiR with various 5,10,15,20-tetrasubstituted porphyrins was investigated. In contrast to OEP, these porphyrins have free β- and occupied *meso* positions and thus some directing effect towards the β positions was expected. Callot had shown that H_2(TPP) **1a** reacts with BuLi in 18% yield to the 23-hydro-5-butyl-5,10,15,20-tetraphenylporphyrin, a phlorin, namely under attack at the *meso* position.[25b,c] In addition, he observed formation of the chlorin **15** (in 7% yield, see Scheme 4), that is, the product of a BuLi addition to a C_b–C_b double bond.

Use of Zn^{II}(TPP) **1c** for reaction with BuLi gave a similar result. However, two chlorins, the mono- and dibutylated products **15** and **16** were obtained in 6.5 and 18% yield, respectively (see Scheme 4). Similar products were described by Krattinger and Callot for the reaction of H_2(TPP) with *t*BuLi.[25c] The constitution of the unusual double addition product **16** was unambiguously proven by single crystal X-ray structural analysis of both the free base **16** and its corresponding zinc(II) complex **17** (see below). Thus, for *meso*-aryl porphyrins both *meso*- and β attack of LiR are possible.



Scheme 4. Reaction of Zn^{II}(TPP) with BuLi. a) 1) BuLi, THF, $-40\,^{\circ}C$; 2) H_2O, 15% HCl. b) $ZnBr_2$, THF.

Reaction of LiR with 5,10,15,20-tetraalkylporphyrins: The conformation of 5,10,15,20-tetraalkylporphyrins can vary from planar to highly ruffled, depending on the steric demand of the *meso*-alkyl group.[26, 40] Thus, the nickel(II) porphyrins **18** and **21** were treated with BuLi to investigate the influence of *meso*-alkyl groups on the reactivity with organolithium reagents. Treatment of the tetrabutylporphyrin **18** with BuLi resulted in the almost quantitative formation of an orange compound with broad absorption maxima at 432 and 524 nm in CH_2Cl_2. Such spectra are typical for a porphodimethene, that is here reaction had occurred exclusively at the *meso* position. The porphodimethene **19** was slowly converted by atmospheric oxygen into an orange-red compound that was different from **19** by 2 amu. Spectroscopic studies revealed this compound to be the novel porphodimethene **20** (Scheme 5) with an exocyclic double bond that is formed via

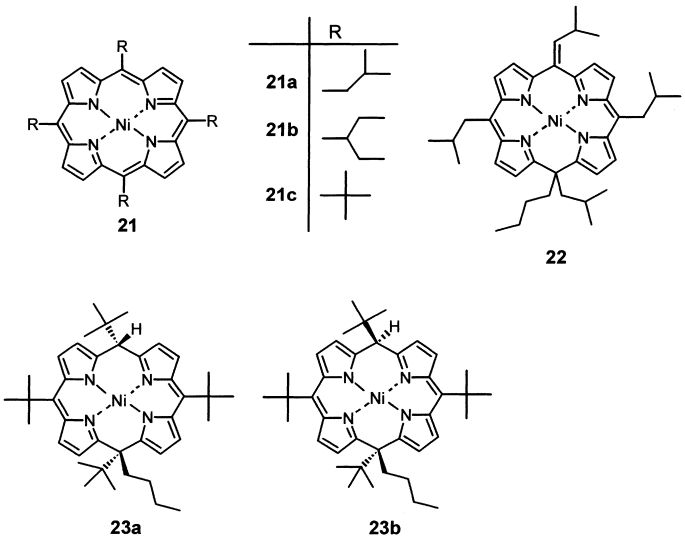


Scheme 5. Reaktion of tetra-*meso* alkylporphyrins with BuLi. a) 1) BuLi, THF, $-40\,^{\circ}C$; 2) H_2O; b) DDQ.

dehydrogenation at the C5 and C5[1] position. Formation of the exocyclic double bond results in a shift of the absorption maxima to 434 and 524 nm. Synthetically, **20** is easily prepared in 80% yield by oxidation of **19** with DDQ.

Similar results were obtained with porphyrins bearing isobutyl (**21a**) or neopentyl (**21b**) residues. For example, reaction of **21a** with BuLi, followed by addition of DDQ without isolation of the intermediary porphodimethene gave the 15[1],15[2]-didehydroporphodimethene **22** in 60% yield. Reaction of the *tert*-butyl porphyrin **21c** with BuLi resulted in the formation of the oxidation stable porphodimethene **23**, whose exact configuration at C5 or C15 (**23a** or **23b**) could not be determined yet. Thus, *meso* alkylporphyrins react with organolithium reagents exclusively at the *meso* positions a further indication for the higher reactivity of the C_m positions towards nucleophilic attack.[47]

Crystallographic studies: As several of the novel porphyrins discussed here have potentially nonplanar macrocycle conformations, extensive crystallographic studies were performed on the compounds described above. Of prime interest was an



investigation of the step by step effect of introduction of successively more *meso*-butyl groups. Selected conformational and structural parameters are compiled in Table 1. Compound **3a** with one *meso*-butyl chain exhibits a ruffled conformation typical for Ni^{II} porphyrins (see Figures 1 and 10). This is evidenced by significant displacements of the C_m positions ($\Delta C_m = 0.69$ Å). These displacements are larger than those observed for the ruffled modification of Ni^{II}(OEP) ($\Delta C_m = 0.51$ Å)[48a] and a localized steric influence of the butyl chain on the conformation is indicated by the significantly larger displacement value for C5 ($\Delta C_5 = 0.87$ Å). These results are in line with those described for other 2,3,5,7,8,12,13,17,18-nonaalkylporphyrins.[18, 48b] The packing in these and related compounds is uneventful and needs not be discussed in detail. However, a recurring theme of nonplanar porphyrins—the incorporation of solvate molecules in the crystal lattice—is already evidenced in the structure of **3a**. This compound forms layers of molecules with the butyl "arms" pointing towards each other. Together with the ruffled macrocycle the latter form a convenient binding cavity that contains a methylene chloride of solvation (Figure 1).

The corresponding free base **3c** exhibits a planar macrocycle (with some wave contribution, not shown). However, steric strain is present in the molecule as indicated by the significant core elongation. As described before, a rectangular elongation of the N4 core is the result of in-plane distortion of the porphyrin, which is the preferred way of steric relief for nona- and decasubstituted *free base* porphyrins.[49] This is accompanied by significant widening of the unsubstituted C_a-C_m-C_a angles compared with the *meso* R quadrant in decasubstituted porphyrins. The present structure shows that even with in-plane distortion some redistribution of the steric strain occurs. Both the substituted C_m position C5 and the opposing *meso* position C15 exhibit C_a-C_m-C_a angles of 123–124°, while the average C_a-C_m-C_a angle for C10 and C20 is 131.3(5)°.

Like many other planar or moderately distorted porphyrin compounds, **3f** forms π-stacked layers in the crystal (Figure 2). The dimeric aggregates are characterized by an interplanar separation of 3.78 Å, a ct–ct distance of 5.464 Å,

0947-6539/00/0615-2726 $ 17.50+.50/0 *Chem. Eur. J.* **2000**, *6*, No. 15

Table 1. Selected bond lengths and structural parameters for some of the porphyrins studied [in Å].

	M–N				⊗ [a]	Ξ [b]	Δ24 [c]	ΔC_m [d]	δC_m subst. [e]	δC_m unsubst. [f]
	M–N21	M–N22	M–N23	M–N24						
3a	1.911(5) av.= 1.906	1.892(5)	1.916(5)	1.905(5)	1.906	0.037	0.338	0.69	0.87	0.63
3c	–	–	–	–	2.086	0.385	0.032	0.03	0.07	0.01
3f	1.913(2) av. = 1.916	1.911(2)	1.917(2)	1.921(2)	1.915	0.051	0.308	0.64	0.82	0.58
3h	1.920(4) av. = 1.924	1.922(4)	1.932(4)	1.922(4)	1.924	0.074	0.263	0.52	0.51	0.52
3i Mol. 1 [g]	–	–	–	–	2.077	0.313	0.039	0.07	0.1	0.06
3i Mol. 2 [g]	–	–	–	–	2.078	0.29	0.042	0.06	0.03	0.04
3k	1.927(3) av. = 1.935	1.934(3)	1.941(3)	1.939(3)	1.936	0.07	0.262	0.52	0.52	0.53
3l	–	–	–	–	2.073	0.308	0.083	0.10	0.14	0.07
6 Mol. 1 [g]	1.908(4) av. = 1.904(4)	1.902(3)	1.908(4)	1.899(3)	1.904	0.089	0.390	0.81	0.83	0.78
6 Mol. 2 [g]	1.890(4) av. = 1.897(4)	1.902(4)	1.891(4)	1.905(4)	1.897	0.1	0.408	0.84	0.86	0.81
7 monocl. Mol. 1 [g]	1.901(4) av. = 1.913(4)	1.910(4)	1.916(4)	1.923(4)	1.913	0	0.365	0.75	0.85	0.65
7 monocl. Mol. 2 [g]	1.899(4) av. = 1.904(4)	1.906(4)	1.902(4)	1.909(4)	1.904	0.01	0.382	0.79	0.90	0.68
7 triclinic	1.899(3) av. = 1.900(3)	1.899(3)	1.895(3)	1.907(3)	1.900	0.01	0.401	0.76	0.86	0.66
8	1.882(3) av. = 1.880(3)	1.873(3)	1.883(3)	1.880(3)	1.879	– 0.05	0.446	0.93	0.97	0.81
9 [51]	av. = 1.873(3)				1.872	n.d.	0.462	1.044	1.044	–
10 Mol. 1 [g]	1.885(4) av. = 1.882(4)	1.889(4)	1.881(4)	1.874(5)	1.881	0.079	0.531	1.16	1.16	–
10 Mol. 2 [g]	1.880(4) av. = 1.884(4)	1.871(4)	1.890(4)	1.895(4)	1.884	0.095	0.544	1.18	1.18	–
11	1.895(3) av. = 1.893(3)	1.890(3)	1.891(3)	1.896(3)	1.892	0.032	0.497	1.087	1.124	0.976
12	–	–	–	–	2.097	0.615	0.014	0.045	0.041	0.051

[a] Core size, average vector length from the geometric center of the four nitrogen atoms to the nitrogen atoms. [b] Core elongation parameter defined as the difference between the vector lengths $(|N21-N22|+|N23-N24|)-(|N22-N23|+|N21-N24|)$. [c] Average deviation of the 24 macrocycle atoms from their least-squares plane. [d] Average deviation of the C_m carbon atoms from the 4N-plane. [e] Average deviation of the substituted C_m carbon atoms from the 4N-plane. [f] Average deviation of the unsubstituted C_m carbon atoms from the 4N-plane. [g] Two crystallographically independent molecules.

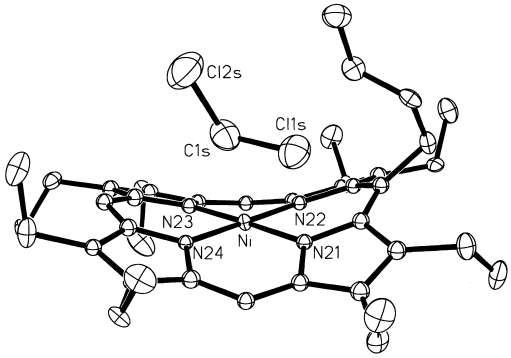


Figure 1. View of the molecular structure of **3a** in the crystal with a solvate methylene chloride loosely bound in the cavity. Thermal ellipsoids are drawn for 50% occupancy, hydrogen atoms have been omitted for clarity.

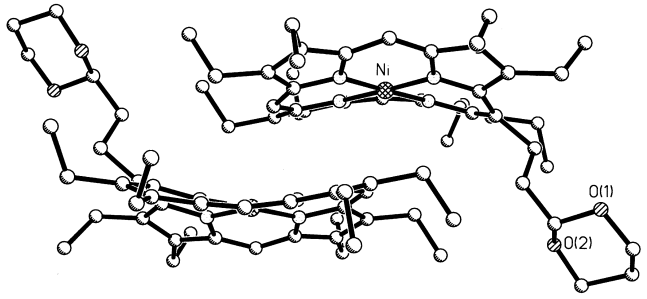


Figure 2. View of the dimeric aggregates formed by **3f** in the crystal. Hydrogen atoms have been omitted for clarity.

a slip angle of 46.2°, and a lateral shift of the metal centers of 3.94 Å.[38e] The conformation is again characterized by overall ruffling with a localized contribution from the C5 phenyl substituent. The magnitude of the difference in displacement values for the substituted and unsubstituted C_m positions is about the same in both alkyl substituted derivatives **3a** and **3f**. In contrast, almost no difference between individual C_m positions is observed for the phenyl derivative **3h** (not shown). The degree of ruffling present in this compound (Table 1) does not exceed that found in the sterically unstrained Ni^{II}(OEP). This compound does not exhibit any in-plane rotation of the *meso*-phenyl group (tilt angle of *meso* aryl with 4N plane 89.4°). As aryl tilt normally correlates with the degree of nonplanarity present in *meso*-aryl porphyrins,[38e] this is another indication that no significant steric strain occurs in compounds of this type. The crystal packing is similar to **3f**, although the interplanar separation is larger.

Similar results were obtained for the related 2,5-dimethoxyphenyl derivative **3k** (tilt angle of *meso* aryl with 4N plane 88.5°, not shown).

The free base **3i** (Figure 3) gave a similar result to that described for **3c**, that is preferential use of in-plane distortion over out-of-plane distortion for relief of steric strain ($\Xi =$ 0.29 – 0.31 Å) and almost no phenyl tilt (tilt angles are 94.7

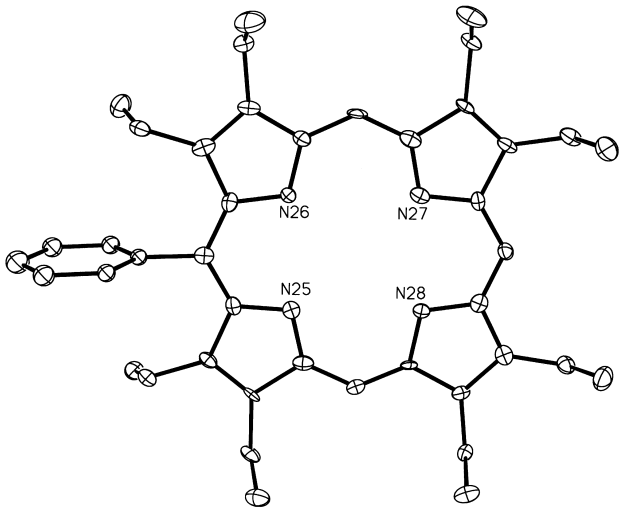


Figure 3. View of the molecular structure of one of the two independent molecules of **3i** in the crystal. Thermal ellipsoids are drawn for 50% occupancy, hydrogen atoms have been omitted for clarity.

and 83.6° for the two crystallographically independent molecules). However, a slight tendency towards saddle distortion is observed. The largest C_b displacements observed were 0.18 Å and might be due to packing effects as the molecules form $\pi-\pi$ aggregates in the crystal. The closely related free base **3l** with a 2,5-dimethoxyphenyl substituent (not shown) exhibits a mixture of in-plane distortion ($\Xi =$ 0.31 Å), slight ruffling ($\Delta C_m = 0.14$ Å) and saddle distortion (C_b displacements of 0.24 Å for C17 and C18).

Figure 4 shows a view of the molecular structure of the 5,15-dibutyl derivative **6** in the crystal. Its conformation is that of a symmetrically ruffled macrocycle with slightly larger displacements for the substituted C_m positions (see Figure 10). The differences between the individual C_m positions are small, an indication for the significant redistribution of steric strain in symmetrically substituted porphyrins. Compound **6** crystallized with two crystallographically independent molecules; both exhibit very similar conformations and structural parameters. The molecular packing in the crystal is characterized by an arrangement in which the macrocycle rings enclose each other with the alkyl chains always pointing towards each other. In effect the areas of nonpolar butyl chains are shielded by the ruffled macrocycles and vice versa.

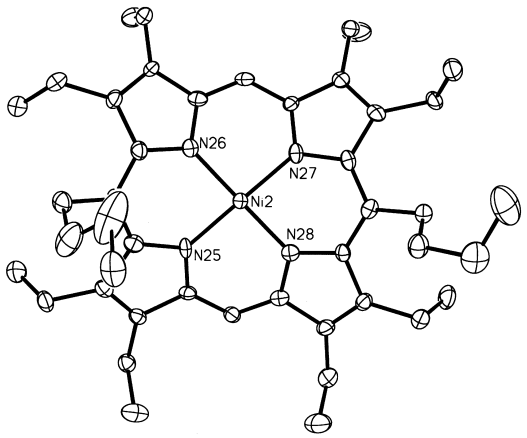


Figure 4. View of the molecular structure of one of the two independent molecules of **6** in the crystal. Thermal ellipsoids are drawn for 50% occupancy, hydrogen atoms and disordered positions have been omitted for clarity.

The regioisomer **7** was crystallized in two different modifications. In line with the 5,10-disubstitution pattern both show more asymmetric distortions.[49b] Compared with **6** the differences in displacements between the substituted and unsubstituted C_m positions are now significant (0.85 – 0.9 vs. 0.65 – 0.68 Å, respectively). In addition, both the monoclinic (not shown) and triclinic (Figure 5) modification are not

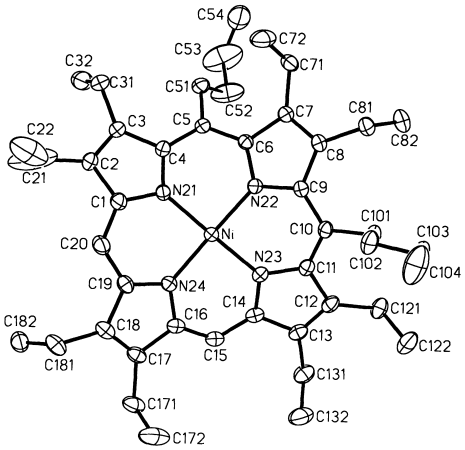


Figure 5. View of the molecular structure of one of the two independent molecules of **7** (triclinic modification) in the crystal. Thermal ellipsoids are drawn for 40% occupancy, hydrogen atoms and disordered positions have been omitted for clarity.

purely ruffled but show out-of-plane tilting for some pyrrole rings (see Figure 10). As other nickel^{II}porphyrins, **7** shows no evidence for rectangular core elongation as described above for some free base porphyrins. Nevertheless, the core conformation is asymmetric as the vector lengths connecting neighboring N–N pairs are shorter by 0.02 – 0.03 Å for the substituted (N21/N22 and N22/N23) quadrants compared to the unsubstituted ones (N23/N24 and N24/N21).

The conformation of the tributylated derivative **8** is again highly ruffled with C_m displacements significantly exceeding those of the porphyrins discussed before.[50] As listed in Table 1, increasing macrocycle distortion in these porphyrins is accompanied by a shortening of the Ni–N bond lengths. Additionally, these structures show the expected effects of macrocycle distortion on trends for increasingly nonplanar porphyrins.[18] Among other effects, increasing ruffling distortion here leads to smaller M-N-C_a [127.1(4)° in **3a** to 126.6(3)° in **8**], larger C_m-C_a-C_b [124.6(5)° in **3a** to 127.1(3)° in **8**], smaller C_a-C_m-C_a angles [121.7(5)° in **3a** to 120.5(3)° in **8**], and longer C_a–C_m bonds [1.389(10) Å in **3a** to 1.404(6) Å in

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8]. These trends are further confirmed when the crystal structure of the tetrabutylated derivative **9** (see Figure 10) is taken into account.[51] Often the relative changes are more pronounced within a given molecule than upon comparison of different molecules. For example, compound **3a**, where one *meso*-butyl group leads to a significantly localized distortion, exhibits average C_a–C_m bond lengths of 1.415(10) Å for the substituted position C5. Compared with an average of 1.381(10) Å for the three unsubstituted C_m positions, this yields a difference of 0.034 Å. In comparison, the overall average of all eight C_a–C_m bonds of 1.389(10) Å in **3a** differs only by 0.02 Å from that of compound **9** [1.409(4) Å]. The various compounds exhibit UV/Vis spectra with absorption maxima that are progressively shifted towards the red with increasing macrocycle distortion. For example, in the series **2b**, **3a**, **6**, **7**, **8**, and **9**[52] the Soret absorption bands are 391, 410, 423, 427, 442, and 459 nm in CH_2Cl_2, respectively. This effect has been noted before[38a] and indicates that similar conformational trends are retained in solution. Structurally, this confirms that varying numbers of *meso*-alkyl substituents can be used in a similar manner as β substituents to yield porphyrins with graded degree of conformational distortion.[54]

Crystal structure analyses of the two porphodimethenes **10** (not shown)[50] and **11** (Figure 6) both establish the *syn*-axial orientation of the *meso*-hydrogen atoms. The presence of the

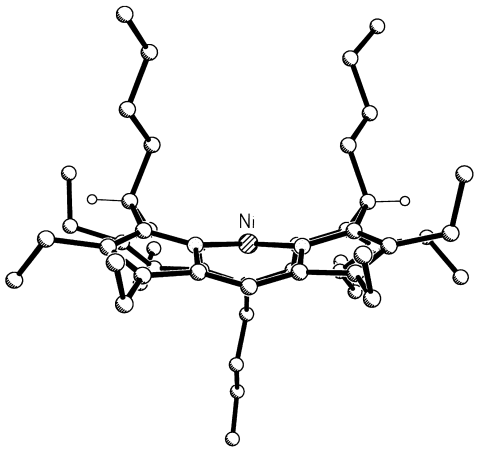

Figure 6. Side view of the molecular structure of **11** in the crystal. Except for *meso* positions hydrogen atoms and have been omitted for clarity.

two sp^3-hybridized *meso* carbon atoms leads to a folding of the macrocycle along the C5–C15 axis. Overall this results in a roof-type structure, namely a mixture of doming and ruffling (see Figure 10) as described before.[15b–d] Only the structure of Ni^{II}(5,15-*syn*-dihydro-5,15-dimethyl-OEP) is directly comparable with the present ones.[53] A comparison of the relevant porphodimethene structures shows that the butyl groups exert additional steric strain in a similar manner as observed in porphyrins. This is evidenced best by the structure of **10** where the C_a-C_m-C_a angles of the two sp^2-hybridized *meso* carbons differ. The one carrying a butyl group has an C_a-C_m-C_a angle of 122.8(4)° while the unsubstituted one has an angle of 124.4(4)°. In addition, the δC_m values are larger for the substituted position (1.12 vs. 0.98 Å) and the tetrabutyl derivative **10** shows absorption maxima (451, 551 nm) slightly more bathochromic than the tributyl derivative **11** (445, 549 nm). Thus, taking the porphodimethene character into account, similar conformational substituent effects are observed in porphyrins and in 5,15-dihydroporphyrins.

The free base **12** (Figure 7) exhibits an almost planar macrocycle with considerable differences in the C_a-C_m-C_a angles for the substituted [124.7(7)°] and unsubstituted *meso*

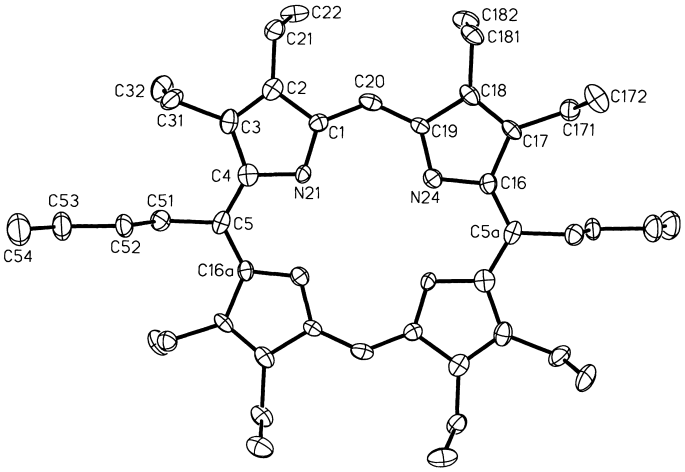

Figure 7. View of the molecular structure of **12** in the crystal. Thermal ellipsoids are drawn for 50% occupancy, hydrogen atoms have been omitted for clarity.

quadrants [132.7(7)°]. This is indicative for in-plane distortion. With a Ξ of 0.615 Å the core elongation is severe and exceeds that observed in other 5,15-disubstituted porphyrins.[49b]

The two crystal structures obtained for the free base chlorin **16** give evidence for the conformational flexibility in chlorins[55] and confirm the structural assignments made before for the double β addition reaction products of free base TPP with alkyl lithium reagents.[25b,c, 28] The unsolvated (Figure 8) and

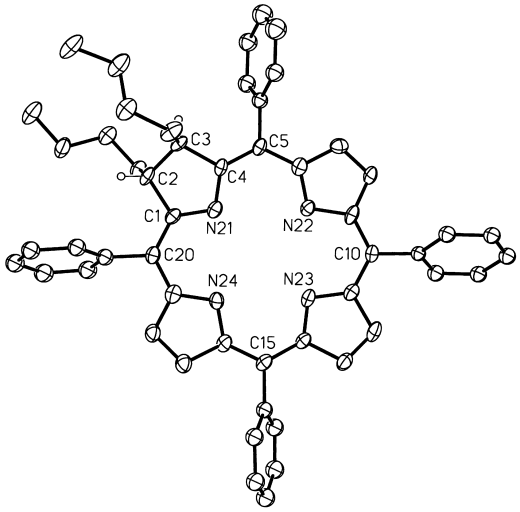

Figure 8. View of the molecular structure of **16** (triclinic unsolvated form) in the crystal. Thermal ellipsoids are drawn for 50% occupancy; except for the C2 and C3 positions, hydrogen atoms have been omitted for clarity.

solvated triclinic modification (not shown) show quite different degrees of conformational distortion ($\Delta 24 = 0.08$ and 0.15 Å) with average C_b displacements for individual pyrrole rings ranging from 0.07 to 0.4 Å. The corresponding zinc(II) complex **17** (Figure 9) shows a similar conformation ($\Delta 24 =$ 0.1 Å) with the largest C_b displacements found for the pyrrolenine ring (0.27 Å) and the pyrrole ring containing N24 (0.31 Å). The core conformational parameters are typical for a five-coordinated zinc(II)chlorins.[55, 56] The axial methanol is hydrogen bonded to another methanol of solvation.

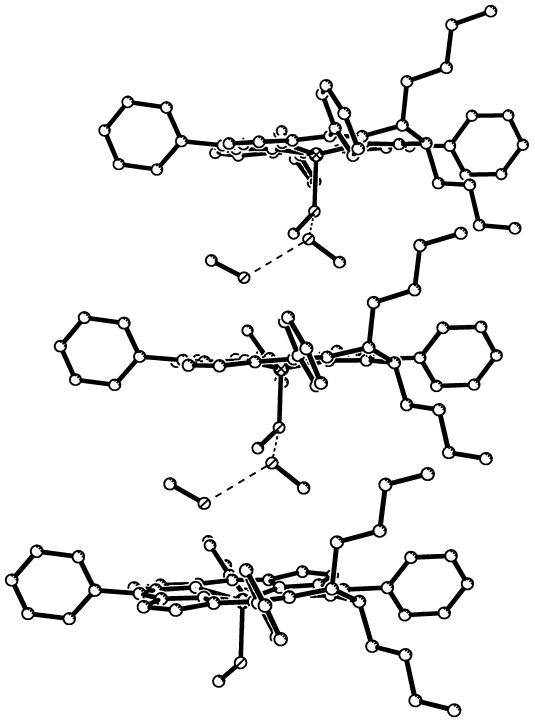

Figure 9. View of the molecular stacks formed by **17(MeOH)** in the crystal. Dashed lines indicate hydrogen bonding; hydrogen atoms have been omitted for clarity. Selected bond lengths and angles: Zn–N(21) 2.112(4) Å, Zn–N(22) 2.056(4) Å, Zn–N(23) 2.099(4) Å, Zn–N(24) 2.043(4) Å, Zn–O(1A) 2.116(3) Å, C(2)–C(3) 1.515(6) Å, C(1)-C(2)-C(3) 101.2(4)°, C(3)-C(2)-C(21) 112.1(4)°, C(1)-C(2)-C(21) 110.5(4)°, C(2)-C(3)-C(4) 102.2(4)°.

and simple synthetic approach to highly substituted porphyrins including those with *meso* alkyl groups and to dodecasubstituted porphyrins with mixed substituent pattern has become possible.

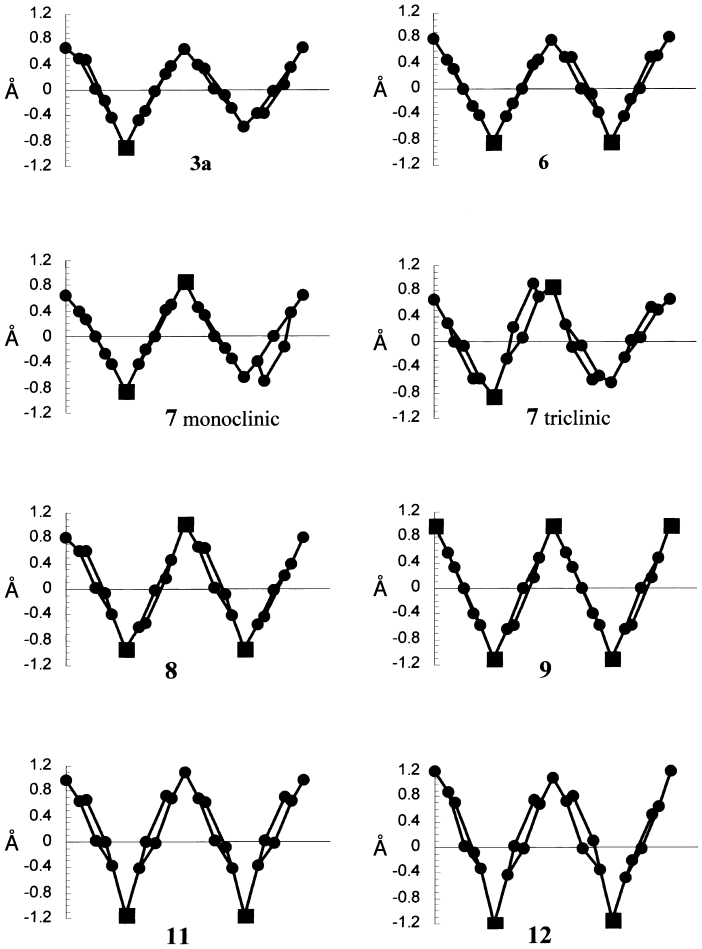

Figure 10. Skeletal deviation plots for selected nonplanar porphyrins. The *x* axis is not to scale and the sequence of pyrrole rings follows the IUPAC nomenclature from left to right (N21, N22, N23, N24). (■ indicates a substituted *meso*-carbon atom for a porphyrin or the sp^3-hybridized *meso*-carbon atoms for porphodimethenes. For compounds **6**, **7**, **10**, and **12** only one of the two crystallographically independent molecules is shown.

Conclusion

The present results clearly show, that porphyrins react readily and often quantitatively with organolithium reagents, preferably at the *meso* position. The use of a variety of different alkyl and aryl lithium reagents for the *meso* modification of porphyrins, and our results from other projects using similar chemistry, indicates that, in principle, any organolithium reagent can be used for the facile *meso* substitution of porphyrins, including residues amenable for further transformations to more complex systems. Mechanistically, the reaction follows an addition – oxidation sequence as indicated by the observation that the initial reaction of the porphyrin with LiR can yield oxidation resistant porphodimethenes. The method described here can be used to prepare mono-, di-, tri-, and tetra-*meso*-functionalized porphyrins. Thus, a rational

The structural studies of several nonplanar porphyrins gave results in line with earlier studies and/or predictions. Notably, mono-5- or di-5,15-substituted free base porphyrins rather exhibited in-plane distortion instead of out-of-plane distortions. The metalloporphyrins showed a dependency of the degree and type of distortion on the number and localization of the *meso* substituents. This indicates that nona- to dodecasubstituted alkylporphyrins follow the same conformational trends and exhibit a behavior similar to other highly substituted porphyrins. The distortion mode contributing most significantly to the macrocycle conformation in *meso* alkylporphyrins was ruffling. The degree of overall distortion correlated with observed bathochromic shifts of the absorption maxima, indicative of highly nonplanar conformations both in solution and in the solid state. Similar results were obtained for the highly substituted porphodimethenes **10** and

0947-6539/00/0615-2730 $ 17.50+.50/0 *Chem. Eur. J.* **2000**, *6*, No. 15

11, both of which showed a *syn*-axial orientation of the *meso*-hydrogen atoms. In addition, crystal structures for the double β-addition products of the reaction of LiR with Zn^{II}(TPP) established an *anti* orientation of the two added butyl residues with respect to the molecular plane.

Experimental Section

General: All chemicals used were of analytical grade and purified before use by distillation. Methylene chloride was dried before use by filtration through basic alumina (grade I); methanol was dried by refluxing over magnesium turnings followed by distillation. All manipulations involving LiR reagents were performed under a purified argon atmosphere by using modified Schlenk techniques with dried and degassed solvents. Melting points are uncorrected and were measured with a Reichert Thermovar apparatus. Silica gel 60 (Merck) or basic alumina (Alfa) (usually Brockmann Grade III, i.e., deactivated with 7.5% water) were used for column chromatography. Analytical thin-layer chromatography (TLC) was carried out using silica gel 60 aluminum plates or alumina 60 (neutral, fluorescence indicator F_{254}) plates (precoated sheets, 0.2 mm thick). Reactions were monitored by TLC and spectrophotometry and were carried out in dimmed light. Proton NMR spectra were recorded at a frequency of 250 MHz (AC 250) or 500 MHz (Bruker, AMX 500). All chemical shifts are given in ppm and have been converted to the δ scale and are referenced against the TMS signal as internal standard. Electronic absorption spectra were recorded with a Specord S10 (Carl Zeiss) spectrophotometer using CH_2Cl_2 as solvent. Mass spectra were obtained using a Varian MAT 711 mass spectrometer. Elemental analyses were performed with a Perkin–Elmer 240-analyzer.

Metallation reactions: Cu^{II}, Ni^{II}, Co^{II}, and Zn^{II} were inserted into free base porphyrins using standard acetate methodology in chlorinated hydrocarbons.[3] Alternatively, Ni^{II} was inserted using nickel acetate and DMF as solvent, while metallation with zinc bromide was often superior to use of zinc acetate.

(5-Butyl-2,3,7,8,12,13,17,18-octaethylporphyrinato)nickel(II) (3a): Ni^{II}(OEP) **2b** (100 mg, 0.17 mmol) was dissolved in 60 mL THF and the solution cooled to $-70\,^{\circ}C$. An *n*-Butyl lithium solution (2 M, 0.3 mL in cyclohexane; 0.6 mmol) was added dropwise within 10 min. After addition of BuLi the cold bath was removed and a mixture of water (1 mL) and THF (5 mL) added dropwise. Subsequently a 0.06 M solution of DDQ in CH_2Cl_2 (10 mL) were added to the cold solution. The mixture was stirred for 20 min and filtered through neutral alumina (grade I). Chromatographic purification was achieved on alumina (grade III) eluting with hexane/CH_2Cl_2 4:1 (*v*/*v*). Recrystallization from CH_2Cl_2/methanol gave red crystals of **3a** in quantitative yield. M.p.: 235 °C; ^{1}H NMR (500 MHz, $CDCl_3$): $\delta = -0.51$ (t, ^3J(H,H) = 7.5 Hz, 3H; butyl-CH_3), 0.85 (m, 4H; butyl-CH_2), 1.68, 1.74, 1.75, 1.85 (each t, ^3J(H,H) = 7.5 Hz, 24H; ethyl-CH_3), 3.79 (br s, 16H; ethyl-CH_2), 4.42 (t, J = 7.5 Hz, 2H; 5-CH_2CH$_2$CH$_2$CH$_3$), 9.32 (s, 1H; 15-*H*), 9.33 (s, 2H; 10,20-*H*); UV/Vis (CH_2Cl_2): λ_{max} (lg ε) = 410 (5.23), 535 (4.02), 572 nm (4.10); MS (80 eV, 350 °C): *m*/*z* (%): 646 (100) $[M]^+$, 323 (18) $[M]^{2+}$; HR-MS [$C_{40}H_{52}N_4Ni$] calcd 646.3546, found 646.3578; $C_{40}H_{52}N_4Ni$ (647.67): calcd C 74.19, H 8.09, N 8.65; found C 73.98, H 7.90, N 8.50.

5-Butyl-2,3,7,8,12,13,17,18-octaethylporphyrin (3c): Free base OEP **2a** (100 mg, 0.19 mmol) was dissolved in THF (50 mL) and cooled to $-70\,^{\circ}C$. BuLi stock solution (2 M, 0.5 mL; 1 mmol) was added dropwise and stirred for 15 min. A mixture of water (1 mL) and THF (5 mL) was added and stirring continued for 5 min. This was followed by addition of DDQ solution (0.06 M, 10 mL) in CH_2Cl_2 to the cold reaction mixture. After stirring for 20 min the reaction mixture was filtered through alumina (grade I) and purified by chromatography on neutral alumina (grade III) eluting with hexane/CH_2Cl_2 1:1 (*v*/*v*). Yield: 55 mg, 50%. Alternatively, **3c** is accessible via demetallation of **3a**. For this, **3a** (30 mg, 46 μmol) was dissolved in concentrated sulfuric acid (5 mL) at room temperature and stirred for 25 min. The reaction mixture was diluted with a saturated solution of sodium acetate (25 mL), extracted with CH_2Cl_2, and washed with water. After drying via filtration through alumina (grade I) column chromatographic purification as described above yielded purple crystals (80%). M.p.: 211 °C; ^{1}H NMR (500 MHz, $CDCl_3$): $\delta = -2.83, -2.77$ (each s, 2H; N*H*), 0.91 (t, ^3J(H,H) = 7.5 Hz, 3H; butyl-CH_3), 1.52 (m, 4H; butyl-CH_2), 1.83, 1.87, 1.88, 1.89 (each t, ^3J(H,H) = 7.5 Hz, 24H; ethyl-CH_3), 3.97–4.14 (m, 16H; ethyl-CH_2), 5.06 (q, 2H; butyl-CH_2), 9.79 (s, 1H; 15-*H*), 10.02 (s, 2H; 10-, 20-*H*); ^{13}C NMR (126 MHz $CDCl_3$): δ = 14.08, 17.82, 18.41, 18.46, 19.65, 19.76, 19.96, 22.73, 23.70, 31.37, 40.42, 94.91, 96.33, 118.79, 120.30, 140.37, 140.64, 140.87, 141.98, 142.35, 143.98, 144.56, 145.55; UV/Vis (CH_2Cl_2+1% NEt_3): λ_{max} (lg ε) = 407 (5.26), 507 (4.20), 540 (3.92), 575 (3.90), 620 nm (3.49); UV/Vis (CH_2Cl_2+1% TFA): λ_{max} (lg ε) = 415 (5.47), 560 (4.20), 600 nm (3.86); MS (80 eV, 150 °C): *m*/*z* (%): 590 (100) $[M]^+$, 547 (16) $[M-C_3H_7]^+$, 295 (12) $[M]^{2+}$; HR-MS [$C_{40}H_{54}N_4$] calcd 646.3546, found 646.3578; $C_{40}H_{54}N_4$ (590.90): calcd C 81.31, H 9.21, N 9.48; found C 81.01, H 8.75, N 9.56.

(5-Butyl-2,3,7,8,12,13,17,18-octaethylporphyrinato)copper(II) (3d): Cu^{II}(OEP) **2d** (100 mg, 0.17 mmol) was dissolved in THF (70 mL) and treated with BuLi at $-20\,^{\circ}C$ as described for **3a** to give red crystals (83 mg, 0.13 mmol, 75%). M.p.: 252 °C; UV/Vis (CH_2Cl_2): λ_{max} (lg ε) = 409 (5.44), 537 (3.85), 571 nm (3.71); MS (80 eV, 200 °C): *m*/*z* (%): 651 (100) $[M]^+$, 608 (16) $[M-C_3H_7]^+$, 326 (8) $[M]^{2+}$; $C_{40}H_{52}N_4Cu \cdot 0.5\,CH_3OH$ (668.45): calcd C 72.77, H 8.14, N 8.38; found C 72.75, H 7.76, N 8.08. A small aliquot was demetallated to the free base and gave a NMR spectrum identical to that of **3c**.

(5-Butyl-2,3,7,8,12,13,17,18-octaethylporphyrinato)cobalt(II) (3e): Co^{II}(OEP) **2e** (100 mg, 0.17 mmol) was dissolved in THF (50 mL) and treated with BuLi at $-70\,^{\circ}C$ as described for **3a** to give red crystals (36 mg, 5.6 μmol, 40%). M.p.: 247 °C; UV/Vis (CH_2Cl_2): λ_{max} (lg ε) = 406 (5.29), 525 (3.79), 563 nm (3.55); $C_{40}H_{52}N_4Co \cdot 0.5\,CH_3OH$ (663.84): calcd C 73.28, H 8.20, N 8.44; found C 73.51, H 7.83, N 8.81. A small aliquot was demetallated to the free base and gave a NMR spectrum identical to that of **3c**.

{5-[2-(1,3-Dioxane-2-yl)ethyl]-2,3,7,8,12,13,17,18-octaethylporphyrinato}-nickel(II) (3f): For the preparation of di-*tert*-butylphenyllithium lithium (0.067 g, 9.6 mmol) was combined with di-*tert*-butylbiphenyl (1g, 4.42 mmol) in THF (5 mL). Immediately after addition of the lithium reagent the solution turned deep blue indicating the formation of the radical anion. The mixture was stirred overnight and used for the preparation of 2-(1,3-dioxane-2-yl)ethyllithium.[35] 2-(2-Bromoethyl)-1,3-dioxolane (0.286 g, 1.47 mmol) was dissolved in dry THF (1 mL), cooled to $-60\,^{\circ}C$ and the di-*tert*-butylphenyllithium solution was added dropwise until the color of the mixture remained light blue. Subsequently, a solution of Ni^{II}(OEP) **2b** (100 mg) in THF (60 mL) was added and the solution stirred for 10 min at $-60\,^{\circ}C$. The reaction mixture was hydrolyzed with a solution of THF (5 mL) and water (1 mL), stirred for 5 min and treated with a solution of DDQ in CH_2Cl_2 (0.06 M, 10 mL). After stirring for an additional 15 min the mixture was filtered through neutral alumina and purified by column chromatography on alumina (grade III, hexane/CH_2Cl_2 2:1, *v*/*v*). After recrystallization from CH_2Cl_2/CH_3OH the product **3f** was obtained as red crystals (85 mg, 0.12 mmol, 70%). M.p.: 258 °C; ^{1}H NMR (500 MHz, $CDCl_3$): δ = 1.07 (d, ^2J(H,H) = 13 Hz, 1H; dioxane-5-H_{eq}), 1.25 (m, 2H; 5^2-*H*), 1.71, 1.781, 1.785, 1.87 (each t, ^3J(H,H) = 7.5 Hz, 24H; CH_3), 1.88 (m, 1H; dioxane-5-H_{ax}), 3.28 (td, J = 13 Hz, ^3J(H,H) = 2.5 Hz, 2H; dioxane-4,6-H_{ax}), 3.71–3.90 (m, 16H; CH_2), 4.63 (t, ^3J(H,H) = 7.5 Hz, 2H; 5^1-*H*), 9.387 (s, 2H; 10-, 20-*H*), 9.389 (s, 1H; 15-*H*); ^{13}C NMR (126 MHz, $CDCl_3$): δ = 17.90, 18.08, 19.49, 22.44, 25.59, 26.21, 66.40, 95.55, 96.35, 100.79, 113.76, 137.55, 139.16, 139.61, 140.06, 142.64, 142.85, 144.09, 145.45; UV/Vis (CH_2Cl_2): λ_{max} (lg ε) = 410 (5.31), 533 (4.08), 572 nm (4.19); MS (80 eV, 280 °C): *m*/*z* (%): 704 (100) $[M]^+$, 352 (2) $[M]^{2+}$; $C_{42}H_{54}N_4O_2Ni$ (705.61): calcd C 71.49, H 7.71, N 7.94; found C 71.43, H 7.51, N 8.22.

{5-(4-Phenoxybut-1-yl)-2,3,7,8,12,13,17,18-octaethylporphyrinato}nickel(II) (3g): Similar to the procedure given for **3h** 4-phenoxybutyl bromide (230 mg, 1 mmol) was treated with di-*tert*-butylphenyl lithium followed by reaction with Ni^{II}(OEP) **2b**(100 mg, 0.17 mmol). Compound **3g** was obtained as red crystals (75 mg, 60%), while 30% of the starting material Ni^{II}(OEP) could be recovered. M.p.: 240 °C; ^{1}H NMR (500 MHz, $CDCl_3$): δ = 1.12, 1.20 (each m, 4H; butyl-5^2-, 5^3-*H*), 1.71, 1.782, 1.786, 1.88 (each t, ^3J(H,H) = 7.5 Hz, 24H; ethyl-CH_3), 3.36 (t, ^3J(H,H) = 6.5 Hz, 2H; butyl-5^4-*H*), 3.84 (br s, 16H; ethyl-CH_2), 4.55 (t, ^3J(H,H) = 6.5 Hz, 2H; butyl-5^1-*H*), 6.48 (dd, ^3J(H,H) = 9 Hz, ^4J = 1 Hz, 2H; $H_{o\text{-phenyl}}$), 6.77 (tt, ^3J(H,H) = 9 Hz, ^4J = 1 Hz, 1H, $H_{p\text{-phenyl}}$), 7.03 (dd, ^3J(H,H) = 9 Hz, 2H; $H_{m\text{-phenyl}}$), 9.37 (s, 2H; 10-, 20-*H*), 9.38 (s, 1H; 15-*H*); ^{13}C NMR (126 MHz, $CDCl_3$): δ = 18.08, 19.53, 22.46, 29.16, 31.35, 31.91, 67.01, 95.61, 96.47, 114.17, 120.20, 129.09, 137.44, 139.22, 139.43, 140.15, 142.74, 142.93, 143.88, 145.53; UV/Vis (CH_2Cl_2): λ_{max} (lg ε) = 410 (5.23), 535 (4.03), 573 nm (4.14); MS (80 eV,

250 °C): *m/z* (%): 738 (100) $[M]^+$; $C_{46}H_{56}N_4ONi$ (739.67): calcd C 74.70, H 7.63, N 7.54; found C 74.31, H 7.63, N 7.54.

(2,3,7,8,12,13,17,18-Octaethyl-5-phenylporphyrinato)nickel(II) (3h): Ni^{II}(OEP) **2b** (100 mg, 0.17 mmol) was dissolved in THF (60 mL). The solution was cooled to −10 °C and treated with a solution of phenyl lithium in cyclohexane (1.8 M, 1.5 mL; 2.7 mmol). The reaction mixture was heated to 35 °C and stirred for 30 min. The reaction product was hydrolyzed by addition of water (1 mL) followed by addition of a solution of DDQ in CH_2Cl_2 (0.06 M, 10 mL). Stirring was continued for 15 min and the mixture filtered through alumina grade I, followed by chromatography on neutral alumina (grade III) eluting with hexane/CH_2Cl_2 3:1 (*v/v*). After recrystallization from CH_2Cl_2/CH_3OH the product **3h** was obtained (75 mg, 68%). M.p.: 226 °C; ^{1}H NMR (500 MHz, $CDCl_3$): $\delta = 0.89$ (t, ^3J(H,H) = 7.5 Hz, 6H; CH_3), 1.68 (t, ^3J(H,H) = 7.5 Hz, 6H; CH_3), 1.76 (t, ^3J(H,H) = 7.5 Hz, 12H; CH_3), 2.59 (q, ^3J(H,H) = 7.5 Hz, 4H; CH_2), 3.75, 3.82, 3.84 (each q, ^3J(H,H) = 7.5 Hz, 12H; CH_2), 7.42–7.70 (m, 3H; H_{phenyl}), 7.98 (m, 2H; H_{phenyl}), 9.49 (s, 1H; 15-*H*), 9.54 (s, 2H; 10-, 20-*H*); UV/Vis (CH_2Cl_2): λ_{max} (lg ε) = 401 (5.27), 523 (4.07), 558 nm (4.33); MS (80 eV, 280 °C): *m/z* (%): 666 (100) $[M]^+$, 333 (8) $[M]^{2+}$; $C_{42}H_{48}N_4Ni \cdot 0.5\,CH_3OH$ (683.58): calcd C 74.68, H 7.37, N 8.20; found C 74.50, H 7.09, N 8.55.

2,3,7,8,12,13,17,18-Octaethyl-5-phenylporphyrin (3i): Free base OEP **2a** (100 mg, 0.19 mmol) was dissolved in THF (40 mL). The solution was cooled to 0 °C and treated with a solution of phenyl lithium in cyclohexane (1.8 M, 1 mL, 1.8 mmol). The reaction mixture was heated to 40 °C and stirred for 15 min. After cooling to 0 °C water (1 mL) was added followed by addition of a solution of DDQ in CH_2Cl_2 (0.06 M, 7 mL). Stirring was continued for 5 min and the mixture filtered through alumina grade I, followed by chromatography on neutral alumina (grade III) eluting with hexane/CH_2Cl_2 2:1 (*v/v*). After recrystallization from CH_2Cl_2/CH_3OH the product **3i** was obtained in quantitative yield. M.p.: 261 °C; ^{1}H NMR (500 MHz, $CDCl_3$): $\delta = -3.61, -3.02$ (each s, 2H; N*H*), 1.15 (t, ^3J(H,H) = 7.5 Hz, 6H; CH_3), 1.85 (t, ^3J(H,H) = 7.5 Hz, 6H; CH_3), 1.91 (t, ^3J(H,H) = 7.5 Hz, 12H; CH_3), 2.74 (q, ^3J(H,H) = 7.5 Hz, 4H; CH_2), 3.97–4.12 (m, 12H; CH_2), 7.60–7.85 (m, 3H; H_{phenyl}), 8.20 (m, 2H; H_{phenyl}), 9.92 (s, 1H; 15-*H*), 10.17 (s, 2H; 10-, 20-*H*); UV/Vis (CH_2Cl_2+1% NEt_3): λ_{max} (lg ε) = 404 (5.32), 503 (4.27), 536 (4.02), 572 (3.99), 622 nm (3.57); (CH_2Cl_2+1% TFA): λ_{max} (lg ε) = 419 (5.56), 560 (4.29), 603sh nm (3.74); MS (80 eV, 250 °C): *m/z* (%): 610 (100) $[M]^+$, 305 (18) $[M]^{2+}$; HR-MS [$C_{42}H_{50}N_4$] calcd 610.4036, found 610.4059; $C_{42}H_{50}N_4 \cdot 0.2\,CH_2Cl_2$ (627.87): calcd C 80.73, H 8.09, N 8.92; found C 80.79, H 7.98, N 8.74. Alternatively, this compound is available via demetallation of **3h** (see demetallation procedure for **3c**) in 90% yield.

{2,3,7,8,12,13,17,18-Octaethyl-5-(4-bromophenyl)porphyrinato}nickel(II) (3j): Dibromobenzene (1 g, 4.24 mmol) was dissolved in THF (20 mL) and cooled to −80 °C and treated dropwise with a solution of butyl lithium in cyclohexane (2 M, 2.12 mL, 4.24 mmol) to yield *p*-bromophenyl lithium.[36] The solution was warmed to room temperature and added over the course of 1 h to a solution of Ni^{II}(OEP) **2b** (100 mg, 0.17 mmol) in THF (80 mL). The temperature of the reaction mixture was raised to 50 °C. Subsequent steps after hydrolysis were as described for **3h** and yielded brown-red needles (52 mg, 0.07 mmol, 40%). M.p.: 256 °C; ^{1}H NMR (500 MHz, $CDCl_3$): $\delta = 0.92$ (t, ^3J(H,H) = 7.5 Hz, 6H; CH_3), 1.70 (t, ^3J(H,H) = 7.5 Hz, 6H; CH_3), 1.77 (t, ^3J(H,H) = 7.5 Hz, 12H; CH_3), 2.65, 3.77 (each q, ^3J(H,H) = 7.5 Hz, 8H; CH_2), 3.84 (m, 8H; CH_2), 7.73, 7.89 (each d, ^2J(H,H) = 8 Hz, 4H; H_{phenyl}), 9.52 (s, 1H; 15-*H*), 9.57 (s, 2H; 10-, 20-*H*); ^{13}C NMR (126 MHz, $CDCl_3$): $\delta = 17.69$, 18.12, 19.57, 21.43, 95.71, 96.60, 122.55, 129.62, 134.70, 138.85, 139.48, 141.11, 143.12, 144.83, 144.97; UV/Vis (CH_2Cl_2): λ_{max} (lg ε) = 401 (5.29), 522 (4.08), 559 nm (4.34); MS (80 eV, 220 °C): *m/z* (%): 746 (100) $[M]^+$, 373 (9) $[M]^{2+}$; $C_{42}H_{47}N_4BrNi$ (746.46): calcd C 67.58, H 6.35, N 7.51; found C 67.90, H 6.11, N 6.63.

{2,3,7,8,12,13,17,18-Octaethyl-5-(1,4-dimethoxyphen-6-yl)porphyrinato}-nickel(II) (3k): For the in situ preparation of 2,5-dimethoxyphenyllithium 1-bromo-2,4-dimethoxybenzene (1 g, 4.6 mmol) was dissolved in THF (5 mL) and cooled to −80 °C.[37] The solution was treated dropwise with a solution of butyl lithium in cyclohexane (2 M, 2.12 mL, 4.8 mmol). The solution was heated to room temperature and, over the course of 1 h added to a solution of Ni^{II}(OEP) **3b** (100 mg, 0.17 mmol) in THF (60 mL) and the temperature of the reaction mixture was raised to 50 °C. After cooling to room temperature the reaction mixture was hydrolyzed with water and a solution of DDQ in CH_2Cl_2 (0.06 M, 10 mL) was added. After stirring for 10 min the mixture was filtered through neutral alumina and chromatographed on alumina (grade III) eluting with hexane/CH_2Cl_2 2:1 (*v/v*) and yielded deep red crystals (85 mg, 0.095 mmol, 60%). M.p.: 242 °C; ^{1}H NMR (500 MHz, $CDCl_3$): $\delta = 0.99$, 1.74 (each t, ^3J(H,H) = 7.5 Hz, 12H; CH_3), 1.807, 1.811 (each t, ^3J(H,H) = 7.5 Hz, 12H; CH_3), 2.79, 2.90 (each m, 4H; 3^1-, 7^1-*H*), 3.62, 3.82 (each s, 3H; OCH_3), 3.68–3.92 (m, 12H; CH_2), 7.07 (each d, ^3J(H,H) = 9 Hz, 1H; 2-H_{phenyl}), 7.25 (dd, ^3J(H,H) = 9 Hz, ^4J(H,H) = 3 Hz, 1H; 3-H_{phenyl}), 7.31 (d, ^4J(H,H) = 3 Hz, 1H; 5-H_{phenyl}), 9.52 (s, 1H; 15-*H*), 9.57 (s, 2H; 10-, 20-*H*); ^{13}C NMR (126 MHz, $CDCl_3$): $\delta =$ 16.80, 18.13, 19.59, 21.20, 55.36, 55.94, 95.48, 96.33, 110.81, 115.18, 121.08, 130.47, 139.21, 139.24, 139.57, 140.64, 142.85, 142.93, 144.81, 145.07, 152.67, 152.93; UV/Vis (CH_2Cl_2): λ_{max} (lg ε) = 401 (5.29), 522 (4.12), 558 nm (4.36); MS (80 eV, 300 °C): *m/z* (%): 726 (100) $[M]^+$, 363 (9) $[M]^{2+}$; $C_{44}H_{52}N_4NiO_2$ (727.61): calcd C 72.63, H 7.20, N 7.70; found C 72.75, H 6.90, N 7.42.

2,3,7,8,12,13,17,18-Octaethyl-5-(1,4-dimethoxyphen-6-yl)porphyrin (3l): Using the procedure described for **3k** free base OEP **2a** (100 mg, 0.19 mmol) was treated with in situ generated 2,5-dimethoxyphenyl lithium and yielded **3l** (35 mg, 27%). Alternatively, this compound is accessible via demetallation of **3k**. Using the procedure given for **3c** this gives **3l** in 90% yield. M.p.: 168 °C; ^{1}H NMR (500 MHz, $CDCl_3$): $\delta = -3.15, -2.97$ (each s, 2H; N*H*), 1.21, 1.87 (each t, ^3J(H,H) = 7.5 Hz, 12H; CH_3), 1.92 (t, ^3J(H,H) = 7.5 Hz, 12H; CH_3), 2.30, 2.90 (each m, 4H; 3^1-, 7^1-*H*), 3.55, 3.88 (each s, 3H; OCH_3), 4.02 (m, 12H; CH_2), 7.13 (d, ^3J(H,H) = 9.5 Hz, 1H; 2-H_{phenyl}), 7.31 (dd, ^3J(H,H) = 9.5 Hz, ^4J(H,H) = 3.5 Hz, 1H; 3-H_{phenyl}), 7.56 (d, ^4J(H,H) = 3.5 Hz, 1H; 5-H_{phenyl}), 9.92 (s, 1H; 15-*H*), 10.16 (s, 2H; 10-, 20-*H*); ^{13}C NMR (126 MHz, $CDCl_3$): $\delta = 17.05$, 18.45, 18.60, 19.73, 19.82, 20.75, 55.40, 55.98, 95.30, 96.56, 110.96, 114.71, 115.18, 121.33, 131.40, 140.78, 141.71, 142.04, 142.36, 142.58, 143.73, 144.21, 145.47, 152.61; UV/Vis (CH_2Cl_2+1% NEt_3): λ_{max} (lg ε) = 404 (5.26), 504 (4.11), 537 (3.89), 571 (3.90), 623 nm (3.44); UV/Vis (CH_2Cl_2+1% TFA): λ_{max} (lg ε) = 413 (5.41), 562 (4.18), 607sh nm (3.69); MS (80 eV, 300 °C): *m/z* (%): 670 (100) $[M]^+$, 335 (24) $[M]^{2+}$; $C_{44}H_{54}N_4O_2 \cdot 0.5\,CH_3OH$ (670.94): calcd C 77.81, H 8.22, N 8.16; found C 77.71, H 7.97, N 7.46.

Butylation of 3a: According to the protocol given for **2b** compound **3a** (100 mg, 0.15 mmol) was combined in THF (30 mL). Column chromatography on alumina (grade III) with hexane/CH_2Cl_2 9:1 (*v/v*) yielded two deep red regioisomeric fractions. The first fraction was **6** (87 mg, 0.12 mmol, 80%) followed by **7** (20 mg, 2.8 μmol, 19%); the compounds were recrystallized from CH_2Cl_2/CH_3OH.

(5,10-Dibutyl-2,3,7,8,12,13,17,18-octaethylporphyrinato)nickel(II) (6): M.p.: 232 °C; ^{1}H NMR (500 MHz, $CDCl_3$): $\delta = 0.60$ (t, ^3J(H,H) = 7.5 Hz, 6H; butyl-CH_3), 0.77 (br s, 4H; butyl-CH_2), 1.05 (m, 4H; butyl-CH_2), 1.69, 1.75, 1.85 (each t, ^3J(H,H) = 7.5 Hz, 24H; ethyl-CH_3), 3.73 (br s, 16H; ethyl-CH_2), 4.27 (t, ^3J(H,H) = 7.5 Hz, 4H; 5,10-CH_2CH$_2$CH$_2$CH$_3$), 9.05 (s, 2H; 15,20-*H*); ^{13}C NMR (126 MHz, $CDCl_3$) $\delta = 13.69$, 17.92, 22.13, 22.21, 23.32, 32.19, 36.92, 95.32, 116.09, 136.29, 137.48, 138.80, 139.28, 142.68, 144.11, 145.49, 146.75; UV/Vis (CH_2Cl_2): λ_{max} (lg ε) = 427 (5.19), 555 (4.09), 595 nm (3.99); MS (80 eV, 210 °C): *m/z* (%): 703 (100) $[M]^+$, 351 (21) $[M]^{2+}$; $C_{44}H_{60}N_4Ni$ (703.68): calcd C 75.10, H 8.59, N 7.96; found C 75.02, H 8.51, N 7.99.

(5,15-Dibutyl-2,3,7,8,12,13,17,18-octaethylporphyrinato)nickel(II) (7): M.p.: 218 °C; ^{1}H NMR (500 MHz, $CDCl_3$): $\delta = 0.53$ (t, ^3J(H,H) = 7.5 Hz, 6H; butyl-CH_3), 0.85 (m, 6H; butyl-CH_2), 0.93 (m, 4H; butyl-CH_2), 1.65, 1.79 (each t, ^3J(H,H) = 7.5 Hz, 24H; ethyl-CH_3), 3.69 (br s, 16H; ethyl-CH_2), 4.29 (t, ^3J(H,H) = 7.5 Hz, 4H; 10,20-CH_2CH$_2$CH$_2$CH$_3$), 9.05 (s, 2H; 10–20-*H*); ^{13}C NMR (126 MHz, $CDCl_3$) $\delta = 13.69$, 17.86, 18.04, 19.31, 22.21, 23.16, 31.06, 37.06, 96.43, 114.26, 136.35, 139.40, 144.23, 144.93; UV/Vis (CH_2Cl_2): λ_{max} (lg ε) = 423 (5.20), 552 (4.00), 595 nm (3.82); MS (80 eV, 210 °C): *m/z* (%): 703 (100) $[M]^+$, 351 (13) $[M]^{2+}$; $C_{44}H_{60}N_4Ni$ (703.68): calcd C 75.10, H 8.59, N 7.96; found C 74.77, H 8.55, N 7.58.

(5,10,15-Tributyl-2,3,7,8,12,13,17,18-octaethylporphyrinato)nickel(II) (8): Compound **6** (100 mg, 0.15 mmol) was dissolved THF (10 mL) and treated rapidly with a solution of BuLi in cyclohexane (2 M, 1 mL, 2 mmol) at −100 °C. At the same temperature a 10% solution of water in THF (1 mL) was added and the mixture stirred for 2 min. The cold mixture was then treated with a solution of DDQ in CH_2Cl_2 (0.06 M, 10 mL) and stirred for an additional 20 min. After warming up the mixture was filtered through neutral alumina (grade I) eluting with CH_2Cl_2. Column chromatography on alumina (grade III) with hexane/CH_2Cl_2 19:1 (*v/v*) gave green red crystals of **8** in quantitative yield after recrystallization from CH_2Cl_2/CH_3OH. M.p.: 255 °C; ^{1}H NMR (500 MHz, $CDCl_3$): $\delta = 0.58$ (t, ^3J(H,H) = 7.5 Hz,

0947-6539/00/0615-2732 $ 17.50+.50/0 *Chem. Eur. J.* **2000**, *6*, No. 15

6H; butyl-CH_3), 0.65 (brs, 2H; butyl-CH_2), 0.97 (brs, 4H; butyl-CH_2), 1.04 (brs, 6H; butyl-CH_2), 1.65, 1.75, 1.78, 1.79 (each t, ^3J(H,H) = 7.5 Hz, 24H; ethyl-CH_3), 3.44–3.52 (m, 16H; ethyl-CH_2), 4.03–4.18 (m, 6H; CH_2CH$_2$CH$_2$CH$_3$), 8.77 (s, 1H; 20-*H*); ^{13}C NMR (126 MHz, $CDCl_3$) δ = 13.69, 17.71, 17.80, 17.88, 19.22, 21.96, 22.06, 23.28, 23.41, 31.55, 32.32, 36.88, 95.30, 115.47, 117.35, 135.60, 136.33, 136.66, 138.83, 144.13, 144.97, 146.37, 146.91; UV/Vis (CH_2Cl_2): λ_{max} (lg ε) = 441 (5.08), 570 (3.91), 613sh nm (3.20); MS (80 eV, 220 °C): *m*/*z* (%): 758 (100) $[M]^+$, 715 (33) $[M - C_3H_7]^+$, 701 (30) $[M - C_4H_9]^+$, 379 (10) $[M]^{2+}$; $C_{44}H_{68}N_4Ni$ (759.78): calcd C 75.88, H 9.02, N 7.37; found C 75.75, H 8.68, N 7.22.

Butylation of 8: Porphyrin **8** (100 mg, 0.13 mmol) was dissolved in THF (30 mL) and cooled to −100 °C. A BuLi solution (2 M, 0.8 mL, 1.6 mmol) was added dropwise and the mixture stirred for 10 min. Subsequently a 10% solution of water in THF (10 mL) was added at −100 °C and the mixture stirred for 5 min. Then a solution of DDQ in CH_2Cl_2 (0.06 M, 10 mL) was added to the cold solution and stirring continued for 20 min. After warming up the mixture was filtered through alumina (grade I). Column chromatography on alumina (grade III) with neat hexane yielded first the tetrabutylated porphyrin **9** (50 mg, 0.06 mmol, 50%) followed by the porphodimethene **10** (40 mg, 0.05 mmol, 40%). Both compounds were recrystallized from CH_2Cl_2/CH_3OH.

{5,10,15,20-Tetrabutyl-2,3,7,8,12,13,17,18-octaethylporphyrinato)nickel(II) (9): M.p.: 254 °C; ^{1}H NMR (500 MHz, $CDCl_3$): δ = 0.59 (t, ^3J(H,H) = 7.5 Hz, 12H; butyl-CH_3), 0.73 (brs, 6H; butyl-CH_2), 1.06 (m, 6H; butyl-CH_2), 1.74 (t, ^3J(H,H) = 7.5 Hz, 24H; ethyl-CH_3), 3.48, 3.58 (each brs, 16H; ethyl-CH_2), 4.03 (m, 6H; butyl-CH_2); ^{13}C NMR (126 MHz, $CDCl_3$) δ = 13.69, 1771, 21.82, 23.34, 31.66, 36.72, 116.59 (4C, 5-, 10-, 15-, 20-C), 135.85, 146.48; UV/Vis (CH_2Cl_2): λ_{max} (lg ε) = 459 (4.93), 591 (3.92), 634 nm (3.56); MS (80 eV, 250 °C): *m*/*z* (%): 814 (100) $[M]^+$, 771 (18) $[M - C_3H_7]^+$, 751 (73) $[M - C_4H_9]^+$, 407 (19) $[M]^{2+}$; $C_{52}H_{76}N_4Ni$ (815.89): calcd C 76.55, H 9.36, N 6.87; found C 76.64, H 9.17, N 7.10.

{5,10,15,20-Tetrabutyl-*syn*-5,15-dihydro-2,3,7,8,12,13,17,18-octaethylporphyrinato)nickel(II) (10): M.p.: 180 °C; ^{1}H NMR (500 MHz, $CDCl_3$): δ = 0.95 (t, ^3J(H,H) = 7.5 Hz, 6H; 5^4-, 15^4-*H*), 0.98 (t, ^3J(H,H) = 7.5 Hz, 6H; 10^4-, 20^4-*H*), 1.03 (t, ^3J(H,H) = 7.5 Hz, 12H; 3^2-, 7^2-, 12^2-, 17^2-*H*), 1.13 (t, ^3J(H,H) = 7.5 Hz, 12H; 2^2-, 8^2-, 12^2-, 18^2-*H*), 1.41–1.55 (m, 12H; 5^2-, 5^3-, 10^3-, 15^2-, 15^3-, 20^3-*H*), 1.82 (m, 2H; 10^2-, 20^2-H), 2.30 (q, ^3J(H,H) = 7.5 Hz, 8H; 3^1-, 7^1-, 13^1-, 17^1-*H*), 2.58 (m, 8H; 2^1-, 8^1- 12^1-, 18^1-*H*), 3.12, (m, 2H; 5^1-, 15^1-*H*), 3.78 (t, ^3J(H,H) = 7.5 Hz, 2H; 5-, 15-*H*); ^{13}C NMR (126 MHz, $CDCl_3$) δ = 14.04, 16.29, 16.52, 17.43, 21.17, 23.08, 23.71, 28.92, 31.33, 36.68, 37.55, 42.74, 129.85, 132.44, 140.90, 148.29, 155.65; UV/Vis (CH_2Cl_2): λ_{max} (lg ε) = 326 (0.04), 451 (4.70), 551 nm (3.83); MS (80 eV, 200 °C): *m*/*z* (%): 816 (40) $[M]^+$, 759 (100) $[M - C_4H_9]^+$, 702 $[M - 2C_4H_9]^+$, 408 (12) $[M]^{2+}$; $C_{52}H_{78}N_4Ni$ (817.92): calcd C 76.36, H 9.61, N 6.85; found C 76.24, H 9.46, N 6.88.

{5,10,15-Tributyl-*syn*-5,15-dihydro-2,3,7,8,12,13,17,18-octaethylporphyrinato)nickel(II) (11): When the reaction of **6** with BuLi was performed at temperatures above −100 °C formation of a brown side product was observed, which was difficult to separate chromatographically from **8**. At temperatures above −30 °C the brown compound **11** was the sole product formed and isolated in quantitative yield. M.p.: 175 °C; ^{1}H NMR (250 MHz, $CDCl_3$): δ = 0.93 (t, ^3J(H,H) = 7.5 Hz, 6H; 5^4-, 15^4-*H*), 0.96 (t, ^3J(H,H) = 7.5 Hz, 3H; 10^4-*H*), 1.013, 1.022 (each t, ^3J(H,H) = 7.5 Hz, 12H; 2^2-, 8^2-, 12^2-, 18^2-H), 1.11 (t, ^3J(H,H) = 7.5 Hz, 12H; 3^2-, 7^2-, 13^2-, 17^2-*H*), 1.43–1.50 (m, 10H; 5^2-, 5^3-, 10^3-,15^2-, 15^3-H), 1.76 (m, 2H; 10^2-H), 2.29 (q, *J* = 7.5 Hz, 8H; 3^1-, 7^1-, 13^1-, 171-*H*), 2.38–2.50, 2.52–2.62 (each m, 8H; 2^1-, 8^1-, 12^1-, 18^1-H), 2.96 (m, 6H; 5^1-, 10^1-, 15^1-H), 3.78 (t, ^3J(H,H) = 7.5 Hz, 2H; 5-, 15-*H*), 6.57 (s, 1H; 20-*H*); UV/Vis (CH_2Cl_2): λ_{max} (lg ε) = 445 (4.75), 549 nm (4.31); MS (80 eV, 220 °C): *m*/*z* (%): 760 (48) $[M]^+$, 703 (100) $[M - C_4H_9]^+$, 646 (29) $[M - 2C_4H_9]^+$, 380 (9) $[M]^{2+}$; $C_{48}H_{70}N_4Ni$ (761.80): calcd C 75.68, H 9.26, N 7.35; found C 75.66, H 8.87, N 7.30.

5,15-Dibutyl-2,3,7,8,12,13,17,18-octaethylporphyrin (12): According to the procedure given for the preparation of **3c**, **12** was prepared in 80% yield via demetallation of **7**. M.p.: 204 °C; ^{1}H NMR (250 MHz, $CDCl_3$): δ = −1.53 (brs, 2H; N*H*), 0.95 (brs, 6H; butyl-CH_3), 1.30–2.13 (m, 32H; butyl-CH_2, ethyl-CH_3), 3.93–4.08 (m, 16H; ethyl-CH_2), 4.93 (t, ^3J(H,H) = 7.5 Hz, 4H; butyl-CH_2), 9.98 (brs, 2H; 10-, 20-*H*); ^{1}H NMR (250 MHz, $CDCl_3$+0.5% TFA, TMS): δ = −1.72 (s, 2H; N*H*), 1.22 (t, ^3J(H,H) = 7.5 Hz, 6H; butyl-CH_3), 1.25, 1.38 (each t, ^3J(H,H) = 7.5 Hz, 24H; ethyl-CH_3), 1.93, 2.46 (each m, 8H; butyl-CH_2), 3.48, 3.64 (each q, *J* = 7.5 Hz, 16H; ethyl-CH_2), 4.63 (t, ^3J(H,H) = 7.5 Hz, 4H; butyl-CH_2), 9.78 (s, 2H; 10-, 20-*H*); UV/Vis (CH_2Cl_2+1% NEt_3): λ_{max} (lg ε) = 414 (5.42), 516 (4.43), 584 (4.10); MS (80 eV, 200 °C): *m*/*z* (%): 646 (100) $[M]^+$, 603 (25) $[M - C_3H_7]^+$, 323 (12) $[M]^{2+}$; HR-MS ($C_{44}H_{62}N_4$): calcd 646.4975, found 646.4930; $C_{44}H_{62}N_4 \cdot 0.33\,CH_2Cl_2$ (675.31): calcd C 78.85, H 9.35, N 8.30; found C 79.08, H 9.31, N 7.65.

{5-Butyl-2,3,7,8,12,13,17,18-octaethyl-10-(1,4-dimethoxyphen-6-yl)porphyrinato}nickel(II) (13): Using the procedure described for **3k** compound **3a** (100 mg, 0.15 mmol) was treated with in situ generated 2,5-dimethoxyphenyl lithium and yielded purple crystals of **13** (60 mg, 0.08 mmol, 50%). 30% of the starting material could be recovered. M.p.: 235 °C; ^{1}H NMR (500 MHz, $CDCl_3$): δ = 0.58 (t, ^3J(H,H) = 7.5 Hz, 3H; butyl-CH_3), 0.60 (t, ^3J(H,H) = 7.5 Hz, 3H; ethyl-CH_3), 0.76, 1.02 (each m, 4H; butyl-CH_2), 1.07 (t, ^3J(H,H) = 7.5 Hz, 3H; ethyl-CH_3), 1.64, 1.69, 1.73, 1.74, 1.85 (each t, ^3J(H,H) = 7.5 Hz, 18H; ethyl-CH$_3$), 2.67, 2.79 (each m, 4H; ethyl-CH_2), 3.64–3.79 (m, 18H; ethyl-CH_2, OCH_3), 4.20 (brs, 2H; butyl-CH_2), 7.03 (m, 1H; 2-H_{phenyl}), 7.19 (dd, ^3J(H,H) = 9.2 Hz, ^4J(H,H) = 3.1 Hz, 1H; 3-H_{phenyl}), 7.56 (d, ^4J(H,H) = 3.5 Hz, 1H; 5-H_{phenyl}), 9.10, 9.19 (each s, 2H; 15-, 20-*H*); ^{13}C NMR (126 MHz, $CDCl_3$): δ = 13.61, 16.14, 16.64, 17.71, 17.90, 18.02, 18.19, 19.30, 19.42, 20.81, 21.10, 22.11, 23.32, 33.45, 36.67, 55.34, 55.92, 94.79, 95.55, 110.77, 113.72, 115.12, 137.96, 138.87, 139.46, 139.81, 140.23, 142.68, 143.10, 143.84, 144.58, 144.95, 145.36, 147.78, 152.67, 153.70; UV/Vis (CH_2Cl_2): λ_{max} (lg ε) = 419 (5.21), 543 (4.02), 585 nm (4.03); MS (80 eV, 300 °C): *m*/*z* (%): 784 (100) $[M]^+$, 391 (24) $[M]^{2+}$; $C_{48}H_{60}N_4O_2Ni$ (784.73): calcd C 73.56, H 7.72, N 7.15; found C 73.53, H 7.67, N 7.02.

{5,10-Dibutyl-2,3,7,8,12,13,17,18-octaethyl-10-(1,4-dimethoxyphen-6-yl)-porphyrinato}nickel(II) (14): Using the procedure described for **3k** porphyrin **6** (100 mg, 0.14 mmol) was treated with in situ generated 2,5-dimethoxyphenyl lithium and yielded purple crystals of **14** (60 mg, 0.08 mmol, 50%). 20% of the starting material could be recovered. M.p.: 224 °C; ^{1}H NMR (250 MHz, $CDCl_3$): δ = 0.58 (t, ^3J(H,H) = 7.5 Hz, 3H; butyl-CH_3), 0.60 (t, ^3J(H,H) = 7.5 Hz, 3H; butyl-CH_3), 0.69 (m, 5H; ethyl-CH_3, butyl-CH_2), 0.78 (m, 2H; butyl-CH_2), 1.01 (t, ^3J(H,H) = 7.5 Hz, 3H; ethyl-CH_3), 1.08 (m, 4H; butyl-CH_2), 1.62, 1.67, 1.68, 1.80, 1.81, 1.84 (each t, ^3J(H,H) = 7.5 Hz, 21H; ethyl-CH$_3$), 2.60–2.73 (m, 4H; ethyl-CH_2), 3.58–3.67 (m, 18H; ethyl-CH_2, OCH_3), 4.18 (m, 4H; butyl-CH_2), 7.02 (m, 1H; 2-H_{phenyl}), 7.16 (dd, ^3J(H,H) = 8.8 Hz, ^4J(H,H) = 2.2 Hz, 1H; 3-H_{phenyl}), 7.56 (m, 1H; 5-H_{phenyl}), 8.90 (s, 1H; 20-*H*); UV/Vis (CH_2Cl_2): λ_{max} (lg ε) = 436 (5.02), 564 (4.09), 585 nm (3.75); MS (80 eV, 300 °C): *m*/*z* (%): 838 (100) $[M]^+$, 419 (14) $[M]^{2+}$; $C_{52}H_{68}N_4O_2Ni$ (839.83): calcd C 73.18, H 8.05, N 6.54; found C 73.26, H 8.35, N 6.69.

Butylation of Zn^{II}(TPP): Zn^{II}(TPP) **1c** (150 mg, 0.23 mmol) was dissolved in THF (20 mL) and cooled to −40 °C. Butyl lithium (2 M, 0.4 mL) solution was added rapidly and the mixture warmed to rt. An additional butyl lithium stock solution (0.3 mL) was added until the reaction of Zn^{II}(TPP) was complete. The reaction mixture was treated with water and in order to complete the demetallation HCl (15% in water) was added. The organic phase was extracted with water and dried via filtration over alumina. This step removes polar side products from the starting material which are retained on the alumina. Final purification was achieved by chromatography on alumina (grade III) using hexane/10% methanol in CH_2Cl_2 as eluant. The first fraction consisted **16** (30 mg, 27 μmol, 18%) and the second fraction of **15** (10 mg, 15 μmol, 6.5%). Use of free base H_2TPP gives the same products in lower yields **15:** M.p.: 218 °C; ^{1}H NMR (500 MHz, $CDCl_3$): δ = −1.41 (s, 2H; N*H*), 0.56 (t, ^3J(H,H) = 7.5 Hz, 3H; CH_3), 0.75, 0.83 (each m, 2H; CH_2), 0.98 (m, 2H CH_2), 1.37, 1.59 (each m, 2H; CH_2), 3.90 (dd, ^3J(H,H) = 1 Hz, ^2J = 17.5 Hz, 1H; 3-H_{syn}), 4.37 (dd, ^3J(H,H) = 9 Hz, ^2J = 17.5 Hz, 1H; 3-H_{anti}), 4.68 (m, 1H; 2-H), 7.60–8.20 (m, 20H; H_{phenyl}), 8.18, 8.20 (each d, *J* = 5 Hz, $H_{pyrrole}$), 8.42 (s, 2H; 12-, 13-H), 8.56, 8.57 (each d, *J* = 5 Hz, 7-, 8-, 17-, 18-H); UV/Vis (CH_2Cl_2+1% NEt_3): λ_{max} (lg ε) = 406sh (5.17), 420 (5.27), 518 (4.21), 547 (4.07), 598 (3.87), 652 nm (4.53); MS (80 eV, 250 °C): *m*/*z* (%): 672 (100) $[M]^+$, 615 (42) $[M - C_4H_9]^+$, 336 (16) $[M]^{2+}$; HR-MS $[C_{48}H_{40}N_4]$ calcd 672.3253, found 672.3258; $C_{48}H_{40}N_4 \cdot 0.25\,CH_3OH$ (680.9): calcd C 85.11, H 6.07, N 8.23; found C 85.27, H 5.84, N 8.27.

***trans*-2,3-Dibutyl-5,10,15,20-tetraphenylchlorin (16)**: M.p.: 246 °C; ^{1}H NMR (500 MHz, $CDCl_3$): δ = −1.42 (s, 2H; N*H*), 0.64 (t, ^3J(H,H) = 7.5 Hz, 6H; CH_3), 0.80–1.21 (m, 8H; CH_2), 1.53, 1.64 (m, 4H; CH_2), 4.34 (dd, ^3J(H,H) = 10 Hz, ^2J = 3 Hz, 2H; 2-, 3-H), 7.60–8.25 (m, 20H; H_{phenyl}), 8.16, 8.5 (each d, ^3J(H,H) = 5 Hz, 4H; 7-, 8-, 17-, 18-H), 8.41 (s, 2H; 12-, 13-H); ^{13}C NMR (126 MHz, $CDCl_3$) δ = 13.83, 22.07, 28.81, 33.80, 51.81, 112.83,

Table 2. Summary of crystal data, data collection and refinement for the crystal structure determinations.

	3a	**3c**	**3f**	**3h**	**3i**	**3k**
chemical formula	$C_{40}H_{52}N_4Ni \cdot CH_2Cl_2$	$C_{40}H_{54}N_4$	$C_{42}H_{54}N_4NiO_2$	$C_{42}H_{48}N_4Ni$	$C_{42}H_{50}N_4 \cdot 2\,CH_2Cl_2$	$C_{44}H_{52}N_4NiO_2$
mol. wt.	732.49	590.78	705.60	667.55	695.79	727.61
crystallization	CH_2Cl_2/CH_3OH	CH_2Cl_2/CH_3OH	CH_2Cl_2/CH_3OH	CH_2Cl_2/CH_3OH	CH_2Cl_2/CH_3OH	$CDCl_3/CH_3OH$
color, habit	red parallelepiped	black irregular block	red cube	red parallelepiped	red block	red cube
crystal size [mm]	$0.4 \times 0.1 \times 0.05$	$0.5 \times 0.25 \times 1$	$0.65 \times 0.65 \times 0.65$	$0.78 \times 0.42 \times 0.13$	$0.35 \times 0.30 \times 0.10$	$0.41 \times 0.36 \times 0.30$
lattice type	orthorhombic	triclinic	monoclinic	triclinic	triclinic	monoclinic
space group	*P*bca	$P\bar{1}$	$P2_1/c$	$P\bar{1}$	$P\bar{1}$	$P2_1/n$
a [Å]	13.664(6)	9.549(4)	12.273(3)	10.808(6)	13.752(7)	14.787(4)
b [Å]	14.916(7)	12.767(6)	16.443(5)	12.527(10)	15.043(7)	13.987(3)
c [Å]	36.765(16)	14.537(7)	18.712(6)	14.743(6)	18.590(7)	18.219(5)
α [°]		91.63(4)		65.16(5)	78.88(4)	
β [°]		103.89(3)	102.57(2)	71.95(4)	87.54(4)	92.04(2)
γ [°]		96.51(3)		78.43(6)	89.32(4)	
V [Å^3]	7493(6)	1706(1)	3686(2)	1717(2)	3770(3)	3766(2)
Z	8	2	4	2	4	4
d_{calcd} [Mg m^{-3}]	1.299	1.150	1.272	1.291	1.226	1.283
μ [mm^{-1}]	2.312	0.507	1.071	1.079	1.811	1.067
T_{max}, T_{min}	0.89, 0.46	0.95, 0.79	0.5, 0.5	0.87, 0.49	0.84, 0.57	0.74, 0.67
T [K]	129	126	126	129	129	129
θ_{max} [°]	57.13	57.04	57.0	57.04	57.04	55.05
collec. reflections	5646	4951	5472	4929	10699	5206
indep. reflections	5044	4614	4974	4622	10179	4726
reflections with $F > 4.0\sigma(F)$	3697	3008	4565	4115	6658	3740
R_{int}	0.0778	0.1083	0.1348	0.1859	0.1190	0.0728
no. of parameters	313	397	442	424	819	460
Δ/ρ_{max} [e Å^{-3}]	0.864	0.382	0.402	1.052	0.721	0.389
$R1$ [$F > 4.0\sigma(F)$]	0.0842	0.0940	0.0426	0.0833	0.0948	0.0525
$wR2$ [$F > 4.0\sigma(F)$]	0.2332	0.2302	0.1090	0.2327	0.2149	0.1270
$R1$ (all data)	0.1202	0.1380	0.0470	0.0929	0.1438	0.0703
$wR2$ (all data)	0.2792	0.2631	0.1119	0.2443	0.2446	0.1376

	3l	**6**	**7** monoclinic	**7** triclinic	**8**	**10**
chemical formula	$C_{44}H_{54}N_4O_2$	$C_{44}H_{60}N_4Ni$	$C_{44}H_{60}N_4Ni \cdot CDCl_3$	$C_{44}H_{60}N_4Ni$	$C_{48}H_{68}N_4Ni \cdot CH_2Cl_2$	$C_{52}H_{88}N_4Ni$
mol. wt.	670.91	703.67	823.04	703.67	844.70	827.97
crystallization	$CDCl_3/CH_3OH$	CH_2Cl_2/CH_3OH	$CDCl_3$/*n*-hexane	CH_2Cl_2/CH_3OH	CH_2Cl_2/CH_3OH	CH_2Cl_2/C_2H_5OH
color, habit	red parallelepiped	red parallelepiped	red block	red plate	red block	red parallelepiped
crystal size [mm]	$0.54 \times 0.28 \times 0.16$	$0.80 \times 0.15 \times 0.10$	$1 \times 1 \times 1$	$1.1 \times 1 \times 0.15$	$0.6 \times 0.4 \times 0.35$	$0.62 \times 0.5 \times 0.24$
lattice type	monoclinic	triclinic	monoclinic	triclinic	monoclinic	triclinic
space group	$P2_1/n$	$P\bar{1}$	$P2_1/c$	$P\bar{1}$	$P2_1/c$	*P'1*
a [Å]	11.044(2)	13.416(6)	23.763(6)	9.609(3)	22.798(9)	12.680(4)
b [Å]	15.371(3)	14.168(7)	14.319(4)	15.218(6)	14.839(5)	18.406(7)
c [Å]	22.218(4)	23.748(13)	25.479(7)	15.338(4)	13.620(4)	22.296(9)
α [°]		90.48(4)		61.24(3)		110.59(3)
β [°]	94.836(14)	99.50(4)	101.93(2)	78.36(2)	93.28(3)	95.37(3)
γ [°]		117.27(3)		89.22(3)		103.62(3)
V [Å^3]	3758(1)	3939(3)	8482(4)	1916.6(11)	4600(3)	4644(3)
Z	4	4	8	2	4	4
d_{calcd} [Mg m^{-3}]	1.186	1.187	1.289	1.219	1.220	1.184
μ [mm^{-1}]	0.563	0.959	0.683	0.542	1.946	0.877
T_{max}, T_{min}	0.75, 0.92	0.91, 0.51	0.55, 0.55	0.92, 0.59	0.55, 0.39	0.81, 0.58
T [K]	129	129	129	129	129	126
θ_{max} [°]	56.34	56.54	30.0	30.0	57.04	56.95
collec. reflections	5501	10979	22357	11807	6828	13155
indep. reflections	4952	10434	20945	11186	6215	12471
reflections with $F > 4.0\sigma(F)$	3660	8514	12456	7728	4757	9253
R_{int}	0.0686	0.0673	0.0455	0.0353	0.1049	0.0714
no. of parameters	452	905	1009	454	360	1014
Δ/ρ_{max} [e Å^{-3}]	0.759	1.291	1.360	1.423	0.561	1.318
$R1$ [$F > 4.0\sigma(F)$]	0.0833	0.0775	0.0941	0.0723	0.0710	0.0831
$wR2$ [$F > 4.0\sigma(F)$]	0.2058	0.2081	0.2027	0.1682	0.1584	0.2081
$R1$ (all data)	0.1113	0.0912	0.1648	0.1140	0.0967	0.1112
$wR2$ (all data)	0.2282	0.2235	0.2412	0.1950	0.1720	0.2285

0947-6539/00/0615-2734 $ 17.50+.50/0 *Chem. Eur. J.* **2000**, *6*, No. 15

Table 2 continued.

	11	**12**	**16** triclinic A	**16** triclinic B	**17**
chemical formula	$C_{48}H_{70}N_4Ni \cdot CH_2Cl_2$	$C_{44}H_{62}N_4$	$C_{52}H_{48}N_4$	$C_{52}H_{48}N_4 \cdot CH_2Cl_2$	$C_{53}H_{50}N_4O_3Zn \cdot 2CH_3OH$
mol. wt.	846.72	646.98	728.94	813.87	888.42
crystallization	CH_2Cl_2/CH_3OH	CH_2Cl_2/CH_3OH	CH_2Cl_2/CH_3OH	CH_2Cl_2/CH_3OH	CH_2Cl_2/CH_3OH
color, habit	red block	red plate	irregular shape	rhombic plate	red plate
crystal size [mm]	$0.6 \times 0.4 \times 0.3$	$0.3 \times 0.2 \times 0.05$	$0.42 \times 0.2 \times 0.2$	$0.52 \times 0.5 \times 0.04$	$0.81 \times 0.2 \times 0.03$
lattice type	monoclinic	monoclinic	triclinic	triclinic	monoclinic
space group	$P2_1/n$	$P2_1/n$	$P\bar{1}$	$P\bar{1}$	$P2_1/n$
a [Å]	14.782(6)	16.536(3)	11.883(1)	11.922(11)	13.897(7)
b [Å]	13.570(5)	13.494(3)	13.155(2)	13.401(10)	8.674(3)
c [Å]	23.697(9)	8.7639(18)	14.040(2)	14.634(11)	38.654(16)
α [°]			85.66(1)	96.86(6)	
β [°]	92.20(3)	97.70(3)	74.89(1)	103.51(6)	92.78(4)
γ [°]			72.03(1)	103.57(6)	
V [Å^3]	4750(3)	1938.0(7)	2015.6(5)	2172(3)	4654(4)
Z	4	2	2	2	4
d_{calcd} [Mg m^{-3}]	1.184	1.109	1.201	1.244	1.268
μ [mm^{-1}]	1.885	0.484	0.536	1.655	1.107
T_{max}, T_{min}	0.57, 0.32	0.86, 0.59	0.9, 0.8	0.94, 0.48	0.97, 0.47
T [K]	126	129	129	128	128
θ_{max} [°]	56.09	56.30	56.07	57.55	55.11
collec. reflections	6835	2795	5566	6205	6661
indep. reflections	6201	2448	5255	5866	5866
reflections with $F > 4.0\sigma(F)$	4919	1409	4381	3836	4099
R_{int}	0.0720	0.1061	0.0532	0.0469	0.0387
no. of parameters	505	217	506	413	569
Δ/ρ_{max} [e Å^{-3}]	0.841	0.567	0.195	0.605	0.501
$R1$ [$F > 4.0\sigma(F)$]	0.0676	0.1204	0.0440	0.1130	0.0579
$wR2$ [$F > 4.0\sigma(F)$]	0.1618	0.2931	0.1190	0.2848	0.1279
$R1$ (all data)	0.0851	0.1861	0.0535	0.1624	0.0956
$wR2$ (all data)	0.1749	0.3317	0.1272	0.3264	0.1486

122.36, 123.70, 126.65, 127.14, 127.39, 127.52, 127.69, 127.79, 131.94, 132.70, 133.87, 134.10, 135.15, 141.18, 142.11, 142.39, 152.40, 169.09; UV/Vis (CH_2Cl_2+1% NEt_3): λ_{max} (lg ε) = 406sh (5.16), 420 (5.30), 519 (4.22), 547 (4.07), 598 (3.85), 652 nm (4.50); UV/Vis (CH_2Cl_2+1% TFA): λ_{max} (lg ε) = 436 (5.28), 640 nm (4.49); MS (80 eV, 250 °C): m/z (%): 728 (100) $[M]^+$, 671 (36) $[M - C_4H_9]^+$, 614 (7) $[M - 2C_4H_9]^+$, 364 (15) $[M]^{2+}$; HR-MS $[C_{52}H_{48}N_4]$ calcd 728.3879, found 728.3892; $C_{52}H_{48}N_4 \cdot 0.5\,CH_3OH$ (745.0): calcd C 84.64, H 6.67, N 7.52; found C 84.89, H 6.51, N 7.53.

(*trans*-2,3-Dibutyl-5,10,15,20-tetraphenylchlorinato)zinc(II) (17): Zinc insertion into **16** using zinc bromide in THF gave **19** (90%). M.p.: 320 °C; ^{1}H NMR (500 MHz, $CDCl_3$): δ = 0.65 (t, ^3J(H,H) = 7.5 Hz, 6H; CH_3), 0.84–1.30 (m, 8H; CH_2), 1.52–1.72 (m, 4H; CH_2), 4.22 (dd, ^3J(H,H) = 10 Hz, ^2J = 3 Hz, 2H; 2-, 3-*H*), 7.56–7.73 (m, 14H; H_{phenyl}), 7.93, 8.06, 8.16 (each m, 6H; $H_{o\text{-}phenyl}$), 8.05,8.48 (each d, ^3J(H,H) = 5 Hz, 4H; 7-, 8-, 17-, 18-*H*), 8.34 (s, 2H; 12-, 13-*H*); UV/Vis (CH_2Cl_2): λ_{max} (lg ε) = 419 (5.24), 591sh (3.76), 621 nm (4.39); MS (80 eV, 250 °C): m/z (%): 790 (100) $[M]^+$, 733 (7) $[M - C_4H_9]^+$, 676 (42) $[M - 2C_4H_9]^+$, 395 (16) $[M]^{2+}$.

(5,5,10,15,20-Pentabutyl-15-hydroporphyrinato)nickel(II) (19): NiTnBuP **18** (100 mg, 0.17 mmol) was dissolved in THF (20 mL), cooled to −40 °C and treated with butyl lithium (2 M, 0.3 mL in cyclohexane). The reaction mixture was stirred for 20 min and then water (1 mL) was added. The solution was filtered through neutral alumina (grade III) and chromatographed on alumina (grade III, hexane/CH_2Cl_2 9:1 *v*/*v*). The porphodimethene **19** was obtained as orange powder (90%, 95 mg, 0.15 mmol). M.p.: 169 °C; ^{1}H NMR (500 MHz, $CDCl_3$): δ = 0.89–1.02 (m, 17H; 5^4-, $4'^4$-, 10^4-, 15^3-, 15^4-, 20^4-*H*), 1.29 (m, 2H; 5^1-, $5'^1$-*H*), 1.39–1.50 (m, 12H; 5^2-, $5'^2$-, 5^3-, 10^3-, 15^2-, 20^3-*H*), 1.75 (m, 4H; 10^2-, 20^2-*H*), 1.99 (m, 2H, 5^2-, $5'^2$-*H*), 2.75 (m, 6H; 10^1-, 15^1-, 20^1-*H*), 3.32 (m, 2H, 5^1-, $5'^1$-*H*), 3.77 (t, ^3J(H,H) = 7.5 Hz, 1H; 15-*H*), 6.10, 6.17, 6.93, 6.96 (each d, ^3J(H,H) = 4.5 Hz, 8H; *β*-*H*); UV/Vis (CH_2Cl_2): λ_{max} (lg ε) = 432 (4.69), 524 nm (4.32); MS (80 eV, 250 °C): m/z (%): 648 (15) $[M]^+$, 591 (100) $[M - C_4H_9]^+$, 534 (15) $[M - 2C_4H_9]^+$, 491 (27) $[M - 2C_4H_9 - C_3H_7]^+$, 324 (6) $[M]^{2+}$; HR-MS ($C_{40}H_{54}N_4Ni$): calcd 648.3702, found 648.3722; $C_{40}H_{54}N_4Ni \cdot 0.25\,CH_2Cl_2$ (662.47): calcd C 72.02, H 8.19, N 8.35; found C 71.96, H 7.55, N 7.92.

(5,5,10,15,20-Pentabutyl-15,15^1-didehydroporphyrinato)nickel(II) (20): This compound is obtained from the reaction leading to **19** when an oxidation step is included after hydrolysis with water. The oxidation was performed by adding a solution of DDQ (0.06 M, 10 mL) in CH_2Cl_2 followed by standard work up as described for **19**. In this case the porphodimethene **20** was obtained as orange-red powder (85 mg, 0.13 mmol, 80%). M.p.: 173 °C; ^{1}H NMR (250 MHz, $CDCl_3$): δ = 0.83–1.05 (m, 15H; 5^4-, $5'^4$-, 10^4-, 15^4-, 20^4-*H*), 1.22 (m, 2H; 5^1-, $5'^1$-*H*), 1.30–1.42 (m, 2H; 5^2-, $5'^2$-*H*), 1.47 (m, 8H; 5^3-, $5'^3$, 10^3-, 20^3-*H*), 1.58 (m, 2H, 15^3-*H*), 1.75 (m, 4H; 10^2-, 20^2-*H*), 2.02 (m, 2H, 5^2-, $5'^2$-*H*), 2.58 (m, 2H; 15^2-H), 2.80 (m, 4H; 10^1-, 20^1-*H*), 2.99 (m, 2H, 5^1-, $5'^1$-*H*), 6.37 (dd, ^3J(H,H) = 6 Hz, ^3J(H,H) = 9 Hz, 1H; 15^1-*H*), 6.22, 6.24, 6.43, 6.45, 7.03, 7.05, 7.07, 7.09 (each d, ^3J(H,H) = 4.5 Hz, 8H; *β*-*H*); UV/Vis (CH_2Cl_2): λ_{max} (lg ε) = 434 (4.59), 524 nm (4.06); MS (80 eV, 250 °C): m/z (%): 646 (23) $[M]^+$, 589 (100) $[M - C_4H_9]^+$, 323 (5) $[M]^{2+}$; HR-MS ($C_{40}H_{52}N_4Ni$) calcd 646.3546, found 646.3574; $C_{40}H_{52}N_4Ni$ (647.57): calcd C 74.19, H 8.09, N 8.65; found C 73.96, H 7.84, N 8.84.

(5-Butyl-15,15^1-didehydro-5,10,15,20-tetrakis(1-methylpropyl)porphyrinato)nickel(II) (22): Following the procedure given for **19** reaction of **21a** (100 mg, 0.17 mmol) with BuLi gave an orange-red powder of **22**(70 mg, 0.11 mmol, 60%). M.p.: 178 °C; ^{1}H NMR (500 MHz, $CDCl_3$): δ = 0.72, 0.78 (each d, ^3J(H,H) = 7 Hz, 6H; isobutyl-5^3-*H*), 0.9 (m, 1H; butyl-5^1-*H*), 0.79 (t, ^3J(H,H) = 7 Hz, 2H; butyl-5^4-*H*), 1.01 (m, 14H; butyl-5^3-*H*, isobutyl-10^3-, 20^3-*H*), 1.02, 1.25 (each d, ^3J(H,H) = 7 Hz, 6H; isobutyl-15^3-*H*), 1.49 (m, 2H; butyl-5^2-*H*), 1.73 (m, 1H; isobutyl-5^2-*H*), 2.09 (m, 5H, butyl-5^1-, 5^2-*H*, isobutyl-10^2-, 20^2-*H*), 2.66 (m, 4H; isobutyl-10^1-, 20^1-*H*), 3.04–3.18 (m, 3H, isobutyl-5^1-, 15^2-*H*), 6.21 (d, ^3J(H,H) = 11 Hz, 1H; 15^1-*H*), 6.24, 6.44, 6.45, 7.02, 7.04, 7.05, 7.08 (each d, ^3J(H,H) = 4.5 Hz, 8H; *β*-*H*); UV/Vis (CH_2Cl_2): λ_{max} (lg ε) = 434 (4.59), 548 nm (4.33); MS (80 eV, 250 °C): m/z (%): 646 (18) $[M]^+$, 589 (100) $[M - C_4H_9]^+$, 323 (7) $[M]^{2+}$; HR-MS $[C_{40}H_{52}N_4Ni]$ calcd 646.3546, found 646.3510; $C_{40}H_{52}N_4Ni \cdot 1.5\,CH_2Cl_2$ (774.97): calcd C 64.32, H 7.15, N 7.23; found C 64.70, H 7.02, N 7.09.

(5-Butyl-5,10,15,20-tetra(*tert*-butyl)-15-hydroporphyrinato)nickel(II) (23): Following the procedure given for **19** porphyrin **21c** (100 mg, 0.17 mmol) yielded (40 mg, 0.06 mmol, 40%). M.p.: 157 °C, ^{1}H NMR (500 MHz,

$CDCl_3$): $\delta = 0.80$ (t, $^3J(H,H) = 7.5$ Hz, 3H; butyl-5^4-*H*), 0.75 – 0.82 (m, 2H; butyl-5^3-*H*), 1.24 (m, 2H; butyl-5^2-*H*), 1.27, 1.41 (each s, 18H; *t*-butyl-5^2-, 15^2-H), 1.70 (s, 18H; *t*-butyl-10^2-, 20^2-*H*), 2.21 (m, 2H; butyl-5^1-*H*), 3.88 (s, 1H; 15-*H*), 6.085 (d, $^3J(H,H) = 4.5$ Hz, 2H; 13-, 17-*H*), 6.225 (d, $^3J(H,H) = 4.5$ Hz, 2H; 3-, 7-*H*), 7.175 (d, $^3J(H,H) = 4.5$ Hz, 2H; 2-, 8-*H*), 7.195 (d, $^3J(H,H) = 4.5$ Hz, 2H; 12-, 18-*H*); UV/Vis (CH_2Cl_2): λ_{max} (lg ε) = 452 (4.47), 534 nm (4.49); MS (80 eV, 250 °C): *m*/*z* (%): 648 (8) $[M]^+$, 591 (100) $[M - C_4H_9]^+$, 535 (100) $[M - 2\ C_4H_9]^+$; HR-MS ($C_{40}H_{54}N_4Ni$) calcd 648.3702, found 648.3721.

Crystallography: The crystals were immersed in hydrocarbon oil (Paraton N), suitable single crystals selected under the microscope, mounted on a glass fiber and placed in the low-temperature N_2 stream on the diffractometer.[57] Intensity data for **7** (monoclinic and triclinic modification) were collected with an Siemens R3m/V diffractometer using graphite monochromated $Mo_{K\alpha}$ radiation ($\lambda = 0.71073$ Å) with ω scans. Intensity data for **3a**, **3c**, **3f**, **3h**, **3i**, **8**, **10**, **16** (triclinic B), were collected with an Syntex $P2_1$ instrument using graphite filtered $Cu_{K\alpha}$ radiation ($\lambda = 1.54178$ Å) with $2\theta - \theta$ scans, while data for **3k**, **3l**, **6**, **11**, **12**, **16** (triclinic A), and **17** were collected using an Siemens P4 diffractometer equipped with a rotating anode (2θ-θ scans, Ni-filtered $Cu_{K\alpha}$ radiation, $\lambda = 1.54178$ Å). The intensities were corrected for Lorentz and polarization effects. Absorption corrections were applied using the program XABS2,[58] extinction effects were disregarded. The structures of **3a**, **3f**, **3h**, **3k**, **6**, **7** (monoclinic and triclinic modification), **8**, and **10** were solved with via a Patterson synthesis followed by structure expansion, while the structures of **3c**, **3i**, **3l**, **11**, **12**, **16** (triclinic A and B), and **17** were solved using direct methods.[59] Refinements were carried out by full-matrix least squares on $|F^2|$ with the program SHELXL-97 using all data.[60] Unless otherwise stated, nonhydrogen atoms were refined with anisotropic thermal parameters. Except for disordered groups, hydrogen atoms were generally placed into geometrically calculated positions and refined using a ridging model. Details for the crystal data, data collection and refinement are given in Table 2.

Crystallographic data (excluding structure factors) for the structures reported in this paper have been deposited with the Cambridge Crystallographic Data Centre as supplementary publication no. CCDC-135222 to CCDC-135236. Data for **8** and **10** were deposited earlier.[28] Copies of the data can be obtained free of charge on application to CCDC, 12 Union Road, Cambridge CB2 1EZ, UK (fax: (+44) 1223-336-033; e-mail: deposit @ccdc.cam.ac.uk).

Refinement details: **3a**: Only the nickel atom, side chain carbon atoms and non-hydrogen solvate atoms were refined with anisotropic thermal parameters. **3c**: One ethyl group was found to be disordered and atom C22 was refined with split positions using free refined occupancies of 0.55 and 0.45, respectively. Hydrogen atoms were treated accordingly. **3h**: Residual electron density was located near the Ni center. **3i**: The phenyl groups were refined as rigid hexagons with isotropic thermal parameters. Hydrogen atoms were added in the riding model to all four pyrrole nitrogen atoms and refined with occupancies of 0.5. The two methylene chloride molecules of solvation both were disordered. One chlorine atom in each solvate molecule was refined with two split positions: Cl1S (0.566), Cl1′ (0.434); Cl3S (0.66), Cl3′ (0.34). No hydrogen atoms were included in the refinement for the solvate molecules. **3i**: One ethyl side chain was disordered and refined with two split positions for C181 and C182, each. Occupancies were determined by refinement to 0.61 and 0.39 and hydrogen atoms were treated accordingly. **6**: Two *n*-butyl chains showed large thermal parameters for the carbon atoms. Accordingly, C5C, C5D and C25D were refined as disordered over two split positions with equal occupancies. Hydrogen atoms were treated accordingly. With the exception of C25′ all nonhydrogen atoms were refined with anisotropic thermal parameters. **7** (monoclinic modification): Residual electron density is located near the Ni center. One of the pyrrole rings in molecule 1 (containing C17 and C18) was disordered. C17, C18 and the associated ethyl side chains were refined as two separate sets of positions with equal occupancies. Hydrogen atoms were included in the riding model accordingly. **7** (triclinic modification): Some of the side chain alkyl groups showed high thermal motion. Atom C54 was refined as disordered over two split positions with occupancies of 0.53 (C54) and 0.47 (C54′), respectively. The residual electron density is located as a single peak near the ethyl group at C2. Attempts to model this group as disordered did not improve the refinement model. **8**: Only the side chain and solvent nonhydrogen atoms were refined with anisotropic thermal parameters. The N, C_a, C_b, and C_m atoms each were refined with a common isotropic thermal parameter. **9**: This compound was crystallized from $CHCl_3/CH_3OH$. However, the crystals were twinned and the best refinement converged only at $R1 \approx 0.15$. Crystal data: $C_{60}H_{76}N_4Ni \cdot 2CHCl_3$, triclinic $P\bar{1}$, $a = 13.509(8)$ Å, $b = 14.213(10)$ Å, $c = 15.460(8)$ Å, $\alpha = 91.72(5)°$, $\beta = 90.43(4)°$, $\gamma = 113.72(4)°$, $Z = 2$. A different crystal form is described elsewhere.[51] **10**: One pyrrole ring and several *n*-butyl chains were disordered or showed high thermal motion. Atoms C2, C2A, C2B, C3, C3A, C3B, C20C, C30C and C30D were refined as disordered over two split positions with equal occupancies. No hydrogen atoms were included in the refinement for the disordered positions. Residual electron density was located in the disordered region. **11**: Atom C10D shows very strong librational movement; refinement with split positions gave no improvement of the overall refinement. **12**: The crystal underwent considerable decay during the data collection (19.8%) what probably accounts for the unsatisfactory *R* values. We were unable to obtain better crystals. **16** (triclinic B): The crystal showed only weak diffraction. The phenyl carbon atoms were refined with isotropic thermal parameters. **17**: No hydrogen atoms were included in the refinement for the solvate methanol molecules and the oxygen atom of the axial methanol.

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