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One-pot synthesis of functionalized, highly substituted porphodimethenes

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Abstract—Treatment of nickel(II)complexes of 2,3,7,8,12,13,17,18-octaethylporphyrin with a combination of organolithium and alkyl iodide reagents gives convenient access to di-, tri-and tetra-*meso*-substituted porphodimethenes with different substituent patterns in a one-pot synthesis. The substituents can possess a variety of functional groups like -I, COOEt and CN. The reaction is stereospecific and gives the target compounds in good yields (50–80%). 5,15-Diarylporphyrins react in a different manner. Upon treatment with *n*-butyllithium followed by addition of alkyl iodides with small residues (e.g. ethyl, cyanomethyl) they undergo a trialkylation yielding e.g. (5-butyl-5,5′,15-triethyl-10,20-diphenylporphyrinato)nickel(II). Highly substituted porphodimethenes can also be prepared in one step and good yield (∼60%) using di-*meso*-2,3,7,8,12,13,17,18-octa-β-substituted porphyrins, LiR and DDQ in good yield (∼60%). The conformations of the synthesized porphodimethenes were investigated via two dimensional NMR, NOE and X-ray crystallographic experiments. © 2001 Published by Elsevier Science Ltd.

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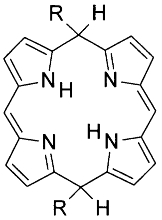
1. Introduction

Porphodimethene, a stable type of 5,15-**1** or 5,10-dihydroporphyrin **2**, is known to be an intermediate between porphyrinogen and porphyrin **3**[1] both in natural and laboratory synthesis.[1a] Only few investigations have appeared in the literature dealing with the chemistry of porphodimethenes. This was mainly due to the absence of suitable syntheses for these compounds.[2] For a long time, the only feasible method to prepare β-substituted porphodimethenes and their metal complexes was Buchler's reductive alkylation, a synthesis limited to the preparation of selected symmetric 5,15-disubstituted porphodimethenes.[3] Recently, several new approaches have been developed, including 2+2 MacDonald condensation reactions.[4] Sessler and coworkers[4b] showed that the acid-catalyzed coupling of mesityldipyrrylmethane with acetone at room temperature gave porphodimethenes—in analogy to the well known porphyrinogen formation from acetone and pyrrole.[5] We have shown that the condensation of sterically hindered aldehydes and pyrrole yields stable porphodimethenes, which could not be oxidized to the porphyrin[6] A quite different methodology started with *meso* substituted porphyrinogens as starting materials that could be converted to calixphyrines after dealkylation.[7] Woodward also used phlorin salts as intermediates that, under strong acidic conditions, were converted to porphodimethenes.[8] Nevertheless, these syntheses are still limited with regard to the preparation of functionalized, β-substituted porphodimethenes. To date, no rational method existed for the synthesis of porphodimethenes with a variety of different *meso* substituents.



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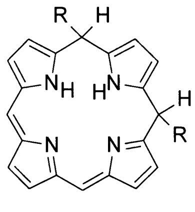

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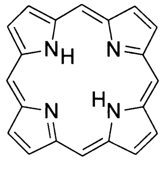

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On the basis of our research on the reaction of porphyrins with organolithium reagents a novel approach seems feasible. There, nucleophilic substitution of porphyrins with LiR proceeds via an intermediary porphodimethene and under special circumstances the formation of

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Keywords: porphodimethenes; lithium and compounds; alkyl iodides; substitution; dihydroporphyrins.

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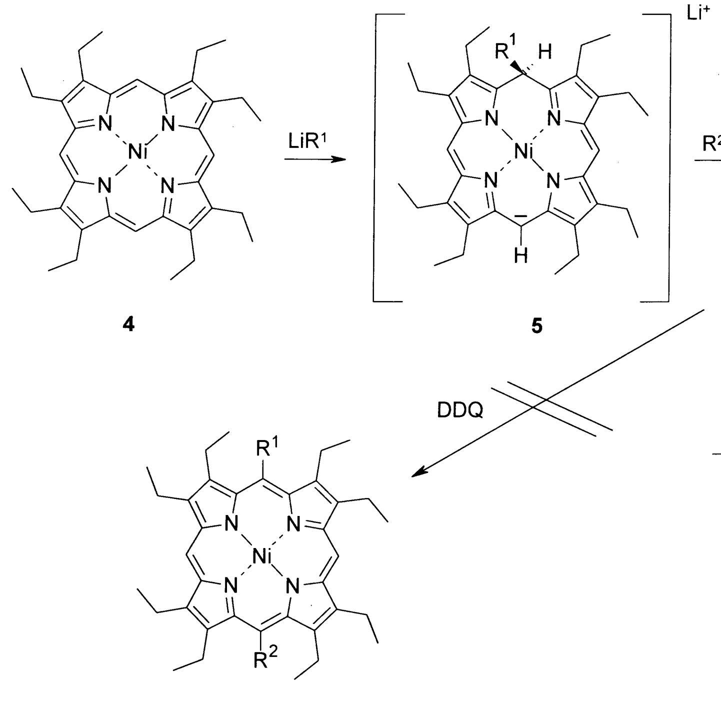


13 R^1 = *n*-Bu, R^2 = *n*-Hex

	R^1	R^2	Yield (%)
6	*n*-Bu	*n*-Hexyl	50
7	*n*-Bu	*n*-Bu	48
8	*n*-Hexyl	$(CH_2)_3CH_2I$	45
9	*n*-Hexyl	$(CH_2)_3CN$	57
10	*n*-Bu	$(CH_2)_4CO_2Et$	63
11	*n*-Hexyl	$(CH_2)_2CH_2I$	22
12	Ph	*n*-Hexyl	37

Scheme 1.

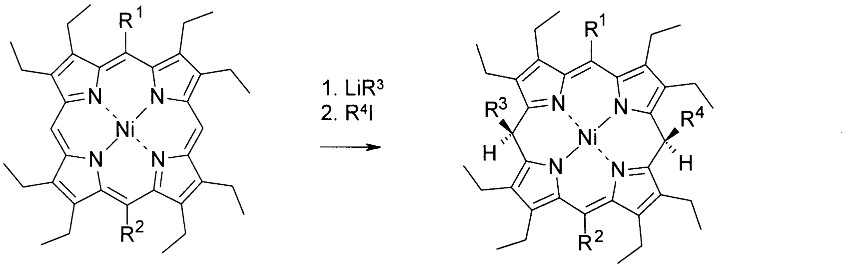
porphodimethenes that are stable towards common oxidants was observed.[9,10] In order to further investigate the chemical, structural, and physical properties of these 'oxidation resistant' dihydroporphyrins, the development of a simple and rational synthesis for such compounds is necessary. Based on the observation that the yield of these 'stable' porphodimethenes was dependent on the reaction conditions used during the nucleophilic substitution of porphyrins with LiR we anticipated that, based on addition reactions of the tetrapyrrole macrocycle with LiR, the development of a general synthesis for porphodimethenes might be possible. Here we report that this is indeed possible by using a combination of LiR^1 and R^2I reagents.

2. Results and discussion

The starting point of our synthesis of porphodimethenes was the observation that porphyrin anions react with alkyl halogenides.[11] For example, we noted that 5,15-disubstituted nickel(II) porphyrins react with LiR under formation of an anion that can be trapped with alkyl halogenides and subsequently be hydrolyzed and oxidized to tetra-*meso* substituted porphyrins. In similar experiments with octaethylporphyrin derivatives we anticipated a trapping of the intermediary anion with electrophiles like *n*-hexyl iodide, resulting in the formation of porphodimethenes. Oxidation of these intermediates to the respective porphyrin would then allow a general synthesis for (2,3,7,8,12,13,17,18-octaethylporphyrinato)nickel(II) [NiOEP, **4**] with two different *meso* substituents. For example, reaction of NiOEP **4** with *n*-butyllithium (*n*-BuLi) and *n*-hexyl iodide (*n*-HexI), followed by oxidation with 2,6-dichloro-5,6-dicyano-1,4-benzenoquinone (DDQ) was expected to yield (5-butyl-2,3,7,8,12,13,17,18-octaethyl-15-hexylporphyrinato)nickel(II) **13**. Surprisingly, the main product isolated *after* oxidation with DDQ was (5-butyl-2,3,7,8,12,13,17,18-octaethyl-15-hexyl-5,15-dihydroporphyrinato)nickel(II) **6**. Obviously, this porphodimethene is stable against oxidants and this indicated the possibility to develop a general route to β-substituted porphodimethenes.

Indeed, reaction of **4** with a variety of LiR^1 and R^2I reagents gave the respective 5,15-substituted porphodimethenes **6–12** in good yields. In general, three to four equivalents of organolithium reagents were used and more than ten equivalents of alkyl iodides. Complete trapping of the anion **5** with electrophiles requires long reaction times (2–12 h) and room temperature. Products like **6**, **7** and **24** were stable against oxidation with DDQ. The most likely reaction mechanism involves reaction of **4** with *n*-BuLi to a phlorin monoanion **5**, that will directly react with electrophilic reagents (Scheme 1).

Thus, a general synthesis of decasubstituted porphodimethenes starting with β-substituted porphyrins in a one-pot reaction is possible. In most cases small amounts of starting material or monosubstituted porphyrins were recovered. The ease of the reaction suggested that a wide variety of alkyl iodide reagents that are stable in basic media at room temperature might be applicable for the synthesis of functionalized porphodimethenes. Therefore, the utility of alkyl iodide reagents with functional groups such as –I, –COOR, –CN was investigated and afforded functionalized porphodimethenes like **8–10** in yields of 45–63%. 1,3-diiodopropane gave the lowest yield (22%), besides formation of the monosubstituted porphyrin **14** and starting material.



	R^1	R^2
14	*n*-Hexyl	H
15	*n*-Bu	H
16	Ph	Ph

	R^1	R^2	R^3	R^4	Yield (%)	
17	*n*-Bu	H	*n*-Hexyl	$(CH_2)_3CN$	65	from **15**
18	Ph	Ph	*n*-Bu	$(CH_2)_5CH_3$	82	from **16**
19	Ph	Ph	*n*-Bu	$(CH_2)_4CO_2Et$	78	from **16**

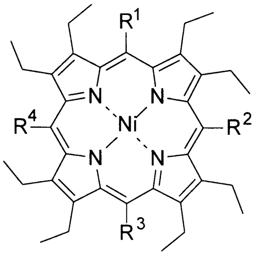
Scheme 2.

The compound **11** was found to be unstable during column chromatography. As expected, aryllithium compounds[9–11] were less reactive and reaction of **4** with phenyllithium, followed by addition of *n*-hexyl iodide gave compound **12** in only 37% yield accompanied by the monophenylated porphyrin. Thus, alkyllithium reagents were used for most of the other transformation described below.

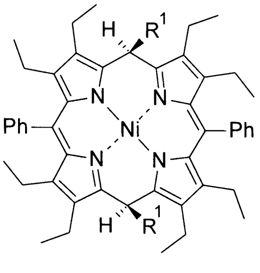
As porphyrins can be substituted with LiR at all four *meso* positions, we utilized this reaction also for the preparation of undeca- and dodecasubstituted porphodimethenes. For example, treatment of the nonasubstituted porphyrin **15** with *n*-hexyllithium, followed by addition of 5-iodovaleronitrile resulted in the formation of the expected undecasubstituted porphodimethene **17** in 65% yield after stirring for five hours. In a similar manner, the decasubstituted porphyrin **16** was treated with *n*-BuLi and, after addition of *n*-hexyl iodide, afforded **18** in 82% yield. Again, alkyl iodide reagents with functional groups as –COOR or –CN could be used. Reaction of *n*-BuLi and ethyl 5-iodovalerate with **16** gave **19** in 78% yield (Scheme 2).

Only decasubstituted porphyrins with *meso*-5,15-disubstitution pattern, e.g. **16**, showed reactivity with the alkyl iodides to form porphodimethenes under the reaction conditions described. In contrast, *meso*-5,10-disubstituted porphyrins reacted to the respective 5,10,15-substituted porphyrins. For example (2,3,7,8,12,13,17,18-octaethyl-5-hexyl-10,15-diphenylporphyrinato)nickel(II) (**21**) was the product of the reaction of **20** with *n*-hexyllithium and *n*-hexyl iodide, besides 52% recovered starting material. As they are less resonance stabilized than 5,15-porphodimethenes, 5,10-porphodimethenes are found only rarely.[12]

Dodecasubstituted porphodimethenes can also be prepared in a one-step reaction using di-*meso* substituted porphyrins, LiR and DDQ. When **16** was treated with *n*-hexyllithium at room temperature and immediately oxidized with DDQ **24** was obtained in 65% yield as the main product, besides the undecasubstituted porphyrin **22**. Here, the monoanion of **16**, obtained after addition of *n*-hexyllithium, is directly oxidized with DDQ to the undecasubstituted porphyrin **22**. This again reacts with *n*-hexyllithium and, after protonation of the resulting anion intermediate, yields the porphodimethene **24**.



20 $R^1 = R^2 = Ph$, $R^3 = R^4 = H$
21 R^1 = *n*-Hexyl, $R^2 = R^3 = Ph$, $R^4 = H$
22 R^1 = *n*-Hexyl, $R^2 = R^4 = Ph$, $R^3 = H$
23 R^1 = *n*-Hexyl, $R^3 = Ph$, $R^2 = R^4 = H$



24 R^1 = *n*-Hexyl

In order to unambiguously determine the stereochemistry and configuration of these porphodimethenes, detailed structural studies were undertaken for (5,15-dibutyl-2,3,7,8,12,13,17,18-octaethyl-5,15-dihydroporphyrinato)-nickel(II) (**7**). For example, the ^{1}H NMR spectrum exhibits two signals for the four enantiotopic and equivalent C_2H_5 groups and one signal each for the 10,20-CH- and 5,15-$CH_2CH_2CH_2CH_3$ groups. The crystal structure of compound **7** showed a *syn*-diaxial orientation (C_{2v}-symmetry) of the *meso*-substituents (Fig. 1). The presence of two *meso*-sp^3 carbons gives rise to a roof-type conformation of the macrocycle. These results agree with known ^{1}H NMR spectra

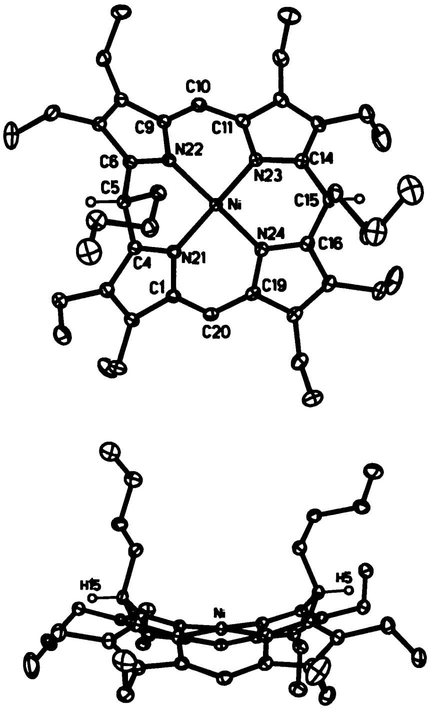


Figure 1. Top and side view of the molecular structure of **7** in the crystal. Only selected hydrogen atoms are shown. Selected bond lengths and angles: Ni–N21 1.902(2) Å, Ni–N22 1.893 (2) Å, Ni–N23 1.884(2) Å, Ni–N24 1.897(2) Å, C4–C5 1.496(3) Å, C5–C6 1.501(3) Å, C14–C15 1.500(3) Å, C15–C16 1.495(3) Å, C4–C5–C6 109.24(2)°, C9–C10–C11 124.5(2)°, C14–C15–C16 110.04(2)°, C19–C20–C1 125.0(2)°.

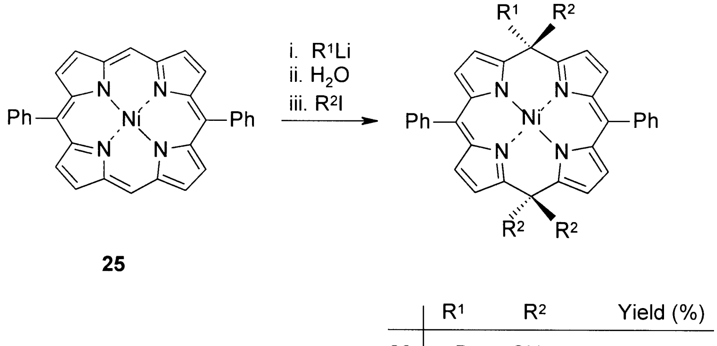
and other X-ray structures of β-substituted porphodimethenes.[3,10]

These results also offer an explanation for the observation of significantly higher yields (~80%) that were obtained in the synthesis of dodecasubstituted porphodimethenes compared to the preparation of decasubstituted porphodimethenes (~50%) and for the former requiring longer reaction time for the trapping of the anion. Obviously, the *meso* substituents already present influence the reaction. Clearly, the regiochemistry of the one-pot reaction of porphyrins with LiR^1 and R^{2}I suggests that the negative charge may be located predominantly at the *meso* position opposite to the LiR attack. On the basis of earlier suggestions by Buchler[3] and our own studies we assume, that the intermediate possesses a conformational structure between phlorin and porphodimethene, more like a dihydroporphyrin. Formation of the distorted conformation is facilitated in decasubstituted porphyrins as they are already conformationally strained.[13] These structural considerations agree with the observed stereospecific insertion of both substituents in the porphyrin macrocycle. If the intermediate has a the roof-type structure, the following electrophilic attack will result in *syn*-diaxial substitution.

Of considerable interest is the question, why some porphodimethenes cannot be oxidized, leading to 'dead ends' in tetrapyrrole chemistry. It is well known that the relief of macrocycle strain in overcrowded porphyrins can be achieved by conversion to the corresponding porphodimethenes.[14] Although the saturated *meso* positions interrupt the macrocycle conjugation, the relative energies of the overcrowded porphyrin and the porphodimethene seem to be similar. In addition, Buchler's investigation has shown that nickel(II), palladium(II), and platinum(II) porphodimethenes are air stable.[3] Use of zinc(II) porphyrins in our reaction procedure gave a variety of products, mainly monosubstituted porphyrin and a variety of green colored bands. The stability of the roof-like porphodimethenes is influenced by the nature of the inserted metal ion. If the central metal ion (e.g. Zn) carries axial ligands the formation of the roof-type structure in the intermediate is sterically hindered.

For example, compounds **6**, **7** and **24** could not be oxidized with DDQ, *p*-chloranil or BBr_3 under standard reaction conditions. 5,15-Dihydroporphyrins like **12** could only be oxidized in very low yields (5%) by adding DBU for the formation of the anion, which could then be oxidized to (2,3,7,8,12,13,17,18-octaethyl-5-hexyl-15-phenylporphyrinato)nickel(II) (**23**) with DDQ at a temperature of 120°C. Under similar reaction conditions, the undeca- and dodecasubstituted porphodimethenes were still stable. Changing the reaction conditions and heating to the boiling point of DMF resulted in the formation of a series of blue polar bands, indicating ring-opened products.

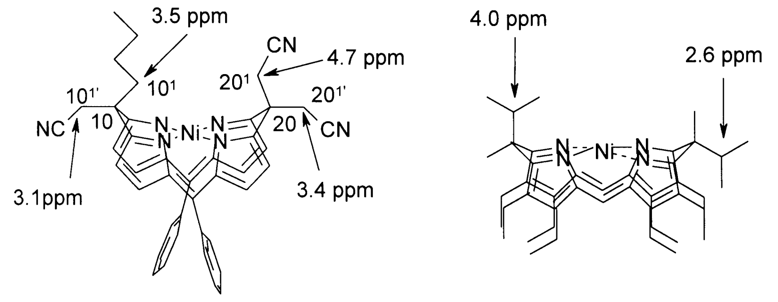
Use of LiR and RI for the preparation of porphodimethenes



25

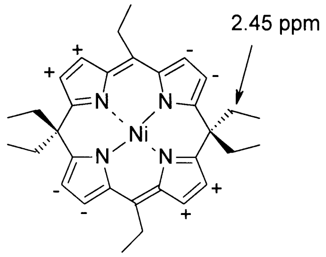
	R^1	R^2	Yield (%)
26	*n*-Bu	CH_3	82
27	*n*-Bu	CH_2CN	78
28	*n*-Bu	$(CH_2)_3CN$	40

Scheme 3.



a roof-shaped

b roof-shaped (Buchler)



c saddle (Floriani)

Figure 2. Representation of different conformations of porphodimethenes with selected ^{1}H NMR data.

is not restricted to β-substituted porphyrin starting materials. Treatment of e.g. (5,15-diphenylporphyrinato)-nickel(II) (**25**) under conditions similar to those described above, normally results in the formation of functionalized *meso* substituted porphyrins in good yields.[11] However, when the substituent R^2 of the alkyl iodides employed is relatively small (e.g. CH_3–, $NCCH_2$–) novel reaction products such as **26** were obtained in about 80% yield. These products were identified as stable porphodimethenes that had undergone multiple substitutions at the C-10 and C-20 positions. For example, reaction of **25** with *n*-BuLi/MeI gave **26** in 82% yield and a reaction using ICH_2CN yielded **27** in 78%. To some extent this reaction can be enforced with larger residues. For example, treatment of **25** with a large excess of R^{2}I (e.g. R=3-cyanopropyl, 40–50 equiv.) at higher temperature (50–60°C) gave **28** in 40% yield. Use of standard conditions with the same reagents resulted in the formation of the tetra-substituted porphyrins as discussed in our earlier work.[11]

The mechanism for the formation of such porphodimethenes might involve a repeated deprotonation of the positions 10 and 20 after formation of the monoanionic intermediate followed by trapping with electrophiles. Surprisingly, the monoanionic porphyrin intermediates resulting from addition of phenyllithium never reacted with alkyl iodides to multiply substituted products like **26–28**. Only the respective tetrasubstituted porphyrins reported in our earlier work were observed as products (Scheme 3).[11]

A spectroscopic investigation supports the structural assignment given for the *meso* trialkylated products. For example, the porphodimethene **27** exhibits the typical UV/Vis-spectrum of a metalloporphodimethene with wide absorption bands at 430 and 535 nm, while the β-proton signals in the ^{1}H NMR spectrum are shifted to high field (6.3 ppm) as a result of the reduced ring current in the porphodimethene system. Interestingly, the substituents derived from the alkyl iodide exhibit greatly different chemical shifts. In compound **27** the two CH_2CN groups at one *meso* position give two singlets at 4.7 and 3.4 ppm. This could be the result of a different spatial orientation with deshielding or shielding fields depending on the *endo* or *exo* orientation in the roof-type conformation described first by Buchler (Fig. 2b).[15] In contrast, Floriani and coworkers[7] have observed identical chemical shifts for the corresponding substituents of (5,5′,10,15,15′,20-hexaethylporphyrinato)-nickel(II) possessing a saddle conformation as shown in Fig. 2c. The split signals of the acetonitrile groups and the molecular peak derived from mass spectrometry indicates the presence of three CH_2CN substituents in **27**, with further confirmation coming from two-dimensional (HMQC) NMR experiments. For example, the $^{1}H–^{13}C$-^{2}J coupling for two CH_2CN groups, proved their location at a common C-atom, while the expected ^{3}J coupling between the two groups has also been observed. The third CH_2CN group exhibited only one ^{1}H NMR singlet at 3.1 ppm, showed a ^{2}J coupling with the *meso* carbon atom and a ^{3}J coupling with a CH_2 group of the *n*-butyl group unit, indicating the presence of a $C_m(CH_2CN)(n\text{-Bu})$ unit. The ^{13}C signals of the 5- and 15-*meso* carbon atoms (δ_C=147 ppm) found in the aromatic region, indicated no additional substituents at these positions.

A NOESY investigation gave further information on the spatial orientation of the *meso* substituents in the porphodimethene **27**. For the $NCCH_2$ groups with ^{1}H signals at 3.1 and 3.4 ppm, large nuclear Overhauser effects (NOE) to the neighboring β-protons resonating at 6.2 ppm were observed (Fig. 3), while the other two *meso* substituents with ^{1}H signals at low field (3.5 and 4.7 ppm) showed no NOE

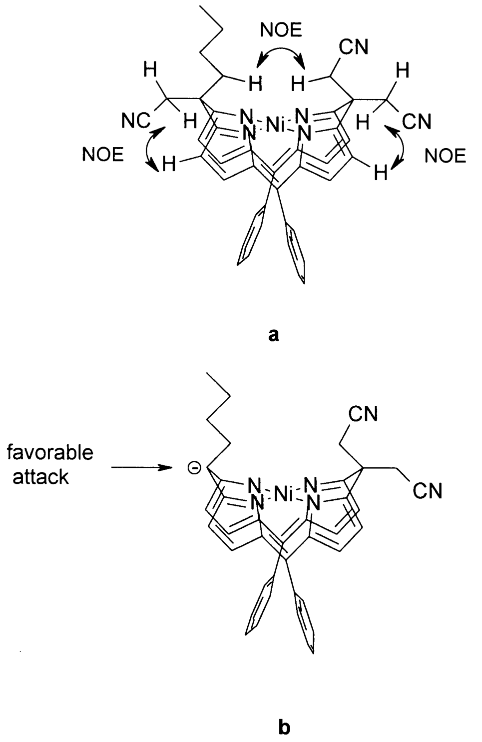


Figure 3. (a) Observed NOE in porphodimethene **26**. (b) Favorable, equatorial attack at the *meso* position of the monoanionic intermediate.

with the β-protons. This indicates that the two acetonitrile groups with an NOE to the β-protons are equatorial substituents, whereas the other two residues suffering more deshielding are axial substituents. The latter two showed a weak NOE between them (see Fig. 3a).

According to the different chemical shifts of the CH_2 groups in the substituents at the 10 and 20 positions in **27**, its structure in solution should be roof-shaped and thus possess a conformation similar to the porphodimethenes reported by Buchler and us. Generally, the axial substituents suffer more deshielding compared to the equatorial substituents,[3] thus the *n*-butyl group in **27** that stemmed from RLi, was assigned as an axial substituent (see Fig. 2). Furthermore, the axial substituents gave a broad signal, an indication for additional interactions, so that they are not rotating freely at room temperature. These broad peaks observed at room temperature changed to relative sharp ones when the temperature was raised (323 K), while a peak broadening was observed at lower temperature (284 K). Interestingly, the present reaction resulted only in the formation of the porphodimethene with the substituent from RLi being in an axial position. No other possible stereoisomers, such as those with the *n*-butyl group in an equatorial orientation, were observed.

The suggestion that porphodimethenes may be effective anion binding agents has led to the synthesis of a variety of new dihydroporphyrin macrocycles.[4] In this context we investigated the relevance of our reaction procedure for free bases. In the case of 2,3,7,8,12,13,17,18-octaethylporphyrin treatment with either phenyllithium and *n*-hexyl iodide or *n*-hexyllithium and methyl iodide gave mainly recovered starting material and monosubstituted free base. As nickel(II)complexes like **7** are acid stable,[3] alternative routes to free base are currently under investigation.

3. Experimental

3.1. General methods

The synthesis of 2,3,7,8,12,13,17,18-octaethylporphyrin,[16] 5,15-diphenylporphyrin[17] and their nickel(II)complexes[18] and the commercially not available compounds were performed using literature procedures. General methods were as described before.[11]

3.2. General procedure for the reaction of β-substituted porphyrins with organolithium reagents and alkyl iodides to porphodimethenes

To a solution of 100 mg **4** (0.17 mmol) in 60 ml THF three to four equivalents of *n*-butyllithium, phenyllithium or *n*-hexyllithium were added at room temperature. After 2–15 min the solution was treated with more than 10 equivalents of alkyl iodide. The reaction mixture was stirred for 2–12 h. After drying under vacuum final purification was achieved via column chromatography on neutral alumina (Brockmann grade III) using dichloromethane/*n*-hexane as eluent. With the exception of porphodimethenes with functional groups like iodide we used dichloromethane/methanol for recrystallization.

3.2.1. (5-Butyl-2,3,7,8,12,13,17,18-octaethyl-15-hexyl-5,15-*syn*-dihydroporphyrinato)nickel(II) (6). To a solution of 100 mg **4** (0.17 mmol) in 60 ml THF 0.15 ml (0.3 mmol) *n*-BuLi was added. After 5 min the solution was treated with 0.05 ml *n*-hexyl iodide (0.34 mmol) and stirred for 12 h. Final purification entailed column chromatography on alumina using dichloromethane/*n*-hexane (1:8, v/v) as eluent. The first red band was identified as the 5,15-dihydroporphyrin **6**, 62 mg (0.085 mmol, 50%) of black crystals, and the second, pink band as starting material **4**, 35 mg (0.052 mmol, 30%); mp 178°C; ^1H NMR (500 MHz, $CDCl_3$, TMS): $\delta=0.89$ (m, 6H, $CH_2CH_2CH_2CH_3$, $CH_2CH_2CH_2CH_2CH_2CH_3$), 1.01 (t, $^3J=7.35$ Hz, 12H, CH_2CH_3), 1.10 (t, $^3J=7.25$ Hz, 12H, CH_2CH_3), 1.45 (m, 12H, $CH_2CH_2CH_2CH_3$, $CH_2CH_2CH_2CH_2CH_2CH_3$), 2.30 (m, 8H, CH_2CH_3), 2.45 (m, 8H, CH_2CH_3), 2.80 (m, 4H, $CH_2CH_2CH_2CH_3$, $CH_2CH_2CH_2CH_2CH_2CH_3$), 3.84 (m, 2H, 5,15-*H*), 6.59 (s, 2H, 10,20-*H*); UV/Vis (CH_2Cl_2): λ_{max} ($\log \epsilon$)=438 nm (4.85), 546 nm (4.44); MS (EI, 80 eV): *m/z* (%): 732 (89) [M^+], 675 (97) [$M^+-C_4H_9$], 647 (91) [$M^+-C_6H_{13}$], 618 (16) [$M^+-C_4H_9-C_6H_{13}-C_2H_5$], 590 (100) [$M^+-C_4H_9-C_6H_{13}-2\times C_2H_5$], 366 (4) [$M^{++}$]; HRMS [$C_{46}H_{66}N_4Ni$]: calcd 732.4641, found 732.4600.

3.2.2. (5,15-Dibutyl-2,3,7,8,12,13,17,18-octaethyl-5,15-*syn*-dihydroporphyrinato)nickel(II) (7). To a solution of 100 mg **4** (0.17 mmol) in 60 ml THF 0.3 ml *n*-butyllithium was added. After 5 min the solution was treated with 0.1 ml *n*-butyl iodide (0.61 mmol) and stirring continued for 12 h. Final purification was achieved via column chromatography on alumina using dichloromethane/*n*-hexane (1:3, v/v) as eluent. The first red band was identified as the 5,15-dihydroporphyrin **7**. After recrystallization from dichloromethane/methanol 58 mg (0.082 mmol, 48%) of dark brown crystals were obtained. A second, pink band contained 32 mg (0.053 mmol, 32%) recovered starting material **4**. Mp 230°C; ^{1}H NMR (500 MHz, $CDCl_3$, TMS): δ=0.92 (t, ^3J=7.3 Hz, 6H, $CH_2CH_2CH_2C\mathit{H}_3$,), 1.03 (t, ^3J=7.26 Hz, 12H, $CH_2C\mathit{H}_3$), 1.10 (t, ^3J=7.16 Hz, 12H, $CH_2C\mathit{H}_3$), 1.44 (m, 8H, $CH_2C\mathit{H}_2C\mathit{H}_2CH_3$), 2.30 (m, 8H, $C\mathit{H}_2CH_3$), 2.46 (m, 8H, $C\mathit{H}_2CH_3$), 2.78 (m, 4H, $C\mathit{H}_2CH_2CH_2CH_3$), 3.80 (t, ^3J=6.97 Hz, 2H, 5,15-*H*), 6.60 (s, 2H, 10, 20-*H*); UV/Vis (CH_2Cl_2): λ_{max} (log ϵ)=438 nm (5.08), 545 nm (4.62); MS (EI, 80 eV): *m/z* (%): 704 (85) [M^+], 647 (100) [$M^+-C_4H_9$], 590 (74) [$M^+-C_4H_9-C_4H_9$], 352 (6) [M^{++}]; HRMS [$C_{44}H_{62}N_4Ni$]: calcd 704.4328, found 704.4372.

3.2.3. {2,3,7,8,12,13,17,18-Octaethyl-15-hexyl-5,15-dihydro-5-(4-iodobutyl)-porphyrinato}nickel(II) (8). A solution of 100 mg **4** (0.17 mmol) in 60 ml THF was stirred with 0.3 ml *n*-hexyllithium for 5 min. Next 0.1 ml 1,4-diiodobutane (5.16 mmol) was added and stirring continued for 12 h. Final purification was achieved via column chromatography on alumina using dichloromethane/*n*-hexane (1:6, v/v) as eluent. The first red band was identified as the 5,15-dihydroporphyrin **8** and gave 66 mg (0.077 mmol, 45%) of dark brown crystals. Starting material **4** (15%) eluted as a second pink band; mp 198°C; ^{1}H NMR (500 MHz, $CDCl_3$, TMS): δ=0.81 (m, 3H, $CH_2CH_2CH_2CH_2CH_2C\mathit{H}_3$), 1.02 (m, 12H, $CH_2C\mathit{H}_3$), 1.09 (t, ^3J=7.46 Hz, 12H, $CH_2C\mathit{H}_3$), 1.29 (m, 4H, CH_2CH_2-$CH_2C\mathit{H}_2C\mathit{H}_2CH_3$, 1.39 (m, 2H, $CH_2CH_2C\mathit{H}_2CH_2CH_2CH_3$), 1.49 (m, 2H, $CH_2C\mathit{H}_2CH_2CH_2CH_2CH_3$), 1.60 (m, 2H, $CH_2C\mathit{H}_2CH_2CH_2I$), 1.93 (m, 2H, $CH_2CH_2C\mathit{H}_2CH_2I$), 2.30 (m, 8H, $C\mathit{H}_2CH_3$), 2.47 (m, 8H, $C\mathit{H}_2CH_3$), 2.79 (m, 4H, $C\mathit{H}_2CH_2CH_2CH_2I$, $C\mathit{H}_2CH_2CH_2CH_2CH_2CH_3$), 3.22 (t, ^3J=7.13 Hz, 2H, $CH_2CH_2CH_2C\mathit{H}_2I$), 3.78 (m, 2H, 5-, 15-*H*), 6.59 (s, 2H, 10-,20-*H*); UV/Vis (CH_2Cl_2): λ_{max} (log ϵ)=438 nm (4.82), 546 nm (4.31); MS (EI, 80 eV): *m/z* (%): 858 (49) [M^+], 773 (37) [$M^+-C_6H_{13}$], 731 (17) [M^+-I], 675 (59) [$M^+-I-C_4H_8$], 646 (23) [$M^+-C_6H_{13}-I$], 590 (100) [[$M^+-I-C_4H_8-C_6H_{13}$, $M^+-C_6H_{13}-I-C_4H_8$] 429 (4) [M^{++}]; HRMS [$C_{46}H_{65}N_4INi$]: calcd 858.3602, found 858.3606.

3.2.4. {5-(3-Cyanopropyl)-2,3,7,8,12,13,17,18-octaethyl-15-hexyl–5,15-dihydroporphyrinato}nickel(II) (9). To a solution of 100 mg **4** (0.17 mmol) in 60 ml THF 0.15 ml (0.3 mmol) *n*-hexyllithium was added and treated with 0.1 ml 5-iodovaleronitrile after 5 min. The reaction mixture was stirred for five hours. Final purification entailed column chromatography on alumina using dichloromethane/*n*-hexane (1:6) as eluent. The first red band was identified as starting material **4** (12%), while the slower moving, major red band contained the 5,15-dihydroporphyrin **9** (72 mg, 0.010 mmol, 57%) as black crystals. Mp 187°C; ^{1}H NMR (500 MHz, $CDCl_3$, TMS): δ=0.85 (t, ^3J=6.93 Hz, 3H, $CH_2CH_2CH_2CH_2CH_2C\mathit{H}_3$), 1.01 (m, 12H, $CH_2C\mathit{H}_3$), 1.09 (t, ^3J=7.55 Hz, 12H, $CH_2C\mathit{H}_3$), 1.27 (m, 4H, CH_2CH_2-$CH_2C\mathit{H}_2C\mathit{H}_2CH_3$), 1.37 (m, 2H, $CH_2CH_2C\mathit{H}_2CH_2CH_2CH_3$), 1.47 (m, 2H, $CH_2C\mathit{H}_2CH_2CH_2CH_2CH_3$), 2.02 (m, 2H, $CH_2C\mathit{H}_2CH_2CN$), 2.29 (m, 8H, $C\mathit{H}_2CH_3$), 2.43 (m, 10H, $CH_2CH_2C\mathit{H}_2CN$, 4×$C\mathit{H}_2CH_3$), 2.74 (m, 2H, $C\mathit{H}_2CH_2$-$CH_2CH_2CH_2CH_3$), 2.83 (m, 2H, $C\mathit{H}_2CH_2CH_2CN$), 3.79 (t, ^3J=7.16 Hz, 1H, 15-*H*), 3.83 (t, ^3J=6.93 Hz, 1H, 5-*H*), 6.60 (s, 2H, 10-,20-*H*); UV/Vis (CH_2Cl_2): λ_{max} (log ϵ)=438 nm (5.05), 646 nm (4.60); MS (EI, 80 eV): *m/z* (%): 743 (93) [M^+], 675 (60) [$M^+-C_4H_6N$], 658 (74) [$M^+-C_6H_{13}$], 646 (10) [$M^+-C_4H_6N-C_2H_5$], 629 (7) [$M^+-C_6H_{13}-C_2H_5$], 590 (100) [$M^+-C_4H_6N-C_6H_{13}$, $M^+-C_6H_{13}-C_4H_6N$], 372 (7) [M^{++}]; HRMS [$C_{46}H_{63}N_5Ni$]: calcd 743.4430, found 743.4437.

3.2.5. {5-Butyl-15-(4-ethoxycarbonylbutyl)-2,3,7,8,12,13,17,18-octaethyl-5,15-dihydroporphyrinato}nickel(II) (10). A solution of 100 mg **4** (0.17 mmol) in 60 ml THF containing 0.15 ml (0.3 mmol) *n*-BuLi was stirred for 3 min treated with 0.1 ml ethyl 5-iodovalerate. After stirring for 5 h the reaction mixture was dried and purified via column chromatography on alumina using dichloromethane/*n*-hexane (1:8, v/v) as eluent. The first red band was identified as the starting material **4** (11%), the next major, red band as the 5,15-dihydroporphyrin **10** (83 mg of black crystals, 0.11 mmol, 63%); mp 208°C; ^{1}H NMR (500 MHz, $CDCl_3$, TMS): δ=0.92 (t, ^3J=7.16 Hz, 3H, $CH_2CH_2CH_2C\mathit{H}_3$), 1.00 (m, 12H, $CH_2C\mathit{H}_3$), 1.09 (t, ^3J=7.48 Hz, 12H, $CH_2C\mathit{H}_3$), 1.19 (t, ^3J=7,16 Hz, 3H, $CH_2CH_2CH_2CH_2CO_2CH_2C\mathit{H}_3$), 1.40–1.49, 1.74 (m, 8H, $CH_2C\mathit{H}_2C\mathit{H}_2CH_3$, $CH_2C\mathit{H}_2C\mathit{H}_2CH_2$-$CO_2CH_2CH_3$), 2.29 (m, 10H, $CH_2CH_2CH_2C\mathit{H}_2CO_2CH_2CH_3$, 8×$C\mathit{H}_2CH_3$), 2.44 (m, 8H, $C\mathit{H}_2CH_3$), 2.77 (m, 4H, $C\mathit{H}_2CH_2CH_2CH_2CO_2CH_2CH_3$, $C\mathit{H}_2CH_2CH_2CH_3$), 3.78 (m, 2H, 5-, 15-*H*), 4.07 (q, ^3J=7.16 Hz, 2H, $CH_2CH_2CH_2$-$CH_2CO_2C\mathit{H}_2CH_3$), 6.59 (s, 2H, 10-, 20-*H*); UV/Vis (CH_2Cl_2):λ_{max} (log ϵ)=438 nm (5.01), 545 nm (4.60); MS (EI, 80 eV): *m/z* (%): 776 (100) [M^+], 719 (66) [$M^+-C_4H_9$], 690 (10) [$M^+-C_4H_8O_2$], 647 (70) [$M^+-C_4H_9-C_4H_8O_2-C_4H_9$], 590 (92) [$M^+-C_4H_9-C_4H_8O_2-C_4H_9-C_4H_9$], 388 (9) [$M^{++}$]; HRMS [$C_{47}H_{66}N_4O_2Ni$]: calcd 776.4539, found 776.4548.

3.2.6. {2,3,7,8,12,13,17,18-Octaethyl-5-hexyl-5,15-dihydro-15-(3-iodopropyl)-porphyrinato}nickel(II) (11). A solution of 100 mg **4** (0.17 mmol) in 60 ml THF was treated with 0.3 ml *n*-hexyllithium. After 5 min 0.1 ml 1,3-diiodopropane (5.42 mmol) was added and stirring continued for 12 h. Column chromatography on alumina using dichloromethane/*n*-hexane (1:6, v/v) as eluent gave the 5,15-dihydroporphyrin **11** (31 mg of dark brown crystals, 0.036 mmol, 22%), besides monosubstitued porphyrin **14** and followed by 15% of the more polar starting material **4**; mp 178°C; ^{1}H NMR (500 MHz, $CDCl_3$, TMS): δ=0.89 (m, 3H, $CH_2CH_2CH_2CH_2CH_2C\mathit{H}_3$), 1.01 (m, 12H, $CH_2C\mathit{H}_3$), 1.09 (m, 12H, $CH_2C\mathit{H}_3$), 1.30–1.42 (m, 8H, $CH_2C\mathit{H}_2C\mathit{H}_2C\mathit{H}_2C\mathit{H}_2CH_3$), 2.22 (m, 2H, $CH_2C\mathit{H}_2CH_2I$), 2.31 (m, 8H, $C\mathit{H}_2CH_3$), 2.47 (m, 8H, $C\mathit{H}_2CH_3$), 2.72 (m, 2H, $C\mathit{H}_2CH_2CH_2CH_2CH_2CH_3$), 2.85 (m, 2H, $C\mathit{H}_2CH_2CH_2I$), 3.51 (t, ^3J=7.3 Hz, 2H, $CH_2CH_2C\mathit{H}_2I$), 3.86 (m, 2H, 5,15-*H*), 6.60 (s, 2H, 10,20-*H*); UV/Vis (CH_2Cl_2):λ_{max} (log ϵ)=437 nm (4.80), 546 nm (4.33); MS (EI, 80 eV): *m/z* (%): 846 (19) [M^+], 718 (17) [M^+-HI], 675 (82)[$M^+-HI-C_3H_7$], 590 (100) [$M^+-HI-C_3H_7-C_6H_{13}$].

3.2.7. (2,3,7,8,12,13,17,18-Octaethyl-5-hexyl-5,15-dihydro-15-phenylporphyrinato)nickel(II) (12). After treatment of a solution of 100 mg **4** (0.17 mmol) in 60 ml THF with 1.5 ml phenyllithium (1.8 M solution in cyclohexane) 0.05 ml hexane iodide was added after 10 min. The reaction mixture was stirred for 12 h and after drying the crude product was chromatographed on alumina eluting with dichloromethane/hexane (1:6, v/v). The major product was obtained as 48 mg of black crystals (0.064 mmol, 37%) of the porphodimethene **12**, besides monosubstituted porphyrin and the more polar starting material **4** (35%). Mp 211°C; ^{1}H NMR (500 MHz, $\mathrm{CDCl_3}$, TMS): $\delta=0.99$ (m, 9H, $2\times\mathrm{CH_2C}\mathit{H}_3$, $\mathrm{CH_2CH_2CH_2CH_2CH_2C}\mathit{H}_3$), 1.10 (t, $^3J=7.16$ Hz, 18H, $\mathrm{CH_2C}\mathit{H}_3$), 1.32–1.49 (m, 8H, $\mathrm{CH_2C}\mathit{H}_2\mathrm{C}\mathit{H}_2\mathrm{C}\mathit{H}_2\mathrm{C}\mathit{H}_2\mathrm{CH_3}$), 2.31 (m, 4H, $\mathrm{C}\mathit{H}_2\mathrm{CH_3}$), 2.47 (m, 12H, $\mathrm{C}\mathit{H}_2\mathrm{CH_3}$), 2.81 (m, 2H, $\mathrm{C}\mathit{H}_2\mathrm{CH_2CH_2CH_2CH_2CH_3}$), 3.80 (t, $^3J=7.26$ Hz, 1H, 5-*H*), 5.21 (t, $^3J=6.97$ Hz, 1H, 15-*H*), 6.61 (s, 2H, 10,20-*H*), 7.51 (m, 1H, $\mathrm{H_{Ph}}$), 7.59 (m, 2H, $\mathrm{H_{Ph}}$), 8.70 (d, $J=3.51$ Hz, 2H, $\mathrm{H_{Ph}}$); UV/Vis ($\mathrm{CH_2Cl_2}$),: $\lambda_{\max}$ ($\log\epsilon$)=438 nm (4.90), 546 nm (4.42); MS (EI, 80 eV): *m/z* (%): 752 (66) [$\mathrm{M^+}$], 667 (100) [$\mathrm{M^+-C_6H_5}$], 376 (12) [$\mathrm{M^{++}}$]; HRMS [$\mathrm{C_{48}H_{62}N_4Ni}$]: calcd 752.4328, found 752.4320.

3.2.8. (2,3,7,8,12,13,17,18-Octaethyl-5-hexylporphyrinato)nickel(II) (14). This compound was obtained as a side product during the synthesis of **11**. The second, red band gave 21 mg of purple crystals (0.031 mmol, 18%). Mp 258°C; ^{1}H NMR (500 MHz, $\mathrm{CDCl_3}$, TMS): $\delta=0.56$ (t, 3H, $\mathrm{CH_2CH_2CH_2CH_2CH_2C}\mathit{H}_3$), 0.70 (m, 2H, $\mathrm{CH_2CH_2CH_2CH_2C}\mathit{H}_2\mathrm{CH_3}$), 0.81 (m, 2H, $\mathrm{CH_2CH_2CH_2C}\mathit{H}_2\mathrm{CH_2CH_3}$), 0.88 (m, 2H, $\mathrm{CH_2CH_2C}\mathit{H}_2\mathrm{CH_2CH_2CH_3}$), 0.95 (m, 2H, $\mathrm{CH_2C}\mathit{H}_2\mathrm{CH_2CH_2CH_2CH_3}$), 1.65 (t, 6H, $^3J=7.28$ Hz, $\mathrm{CH_2C}\mathit{H}_3$), 1.74 (m, 12H, $\mathrm{CH_2C}\mathit{H}_3$), 1.78 (t, 6H, $^3J=7.26$ Hz, $\mathrm{CH_2C}\mathit{H}_3$), 3.79 (m, br., 16H, $\mathrm{C}\mathit{H}_2\mathrm{CH_3}$), 4.35 (m, 2H, $\mathrm{C}\mathit{H}_2\mathrm{CH_2CH_2CH_2CH_2CH_3}$), 9.27 (m, 3H, 10-, 15-, 20-*H*), UV/Vis ($\mathrm{CH_2Cl_2}$) 411 nm (5.22), 533 nm (4.06), 571 nm (4.09), 641 (3.43). MS (EI, 80 eV): *m/z* (%): 674 (100) [$\mathrm{M^+}$], 647 (2) [$\mathrm{M^+-C_2H_5}$], 337 (6) [$\mathrm{M^{++}}$]; HRMS [$\mathrm{C_{42}H_{56}N_4Ni}$]: calcd 674.3859, found 674.3892.

3.2.9. {5-Butyl-10-(3-cyanopropyl)-2,3,7,8,12,13,17,18-octaethyl-20-hexyl-10,20-dihydroporphyrinato}nickel(II) (17). To a solution of 100 mg **15** (0.15 mmol) in 50 ml THF 0.15 ml (0.3 mmol) *n*-hexyllithium was added. After 5 min the solution was treated with 0.5 ml 5-iodovaleronitrile (2.4 mmol) and stirring continued for 2 h. Final purification was achieved via column chromatography on alumina using dichloromethane/*n*-hexane (1:2, v/v) as eluent. The major red band was identified as the 5,15-dihydroporphyrin **17** and gave (90 mg of black crystals, 0.11 mmol, 65%). Mp 208°C; ^{1}H NMR (500 MHz, $\mathrm{CDCl_3}$, TMS): $\delta=0.85$, 0.95 (t, $^3J=7.28$ Hz, t, $^3J=6.78$ Hz, 3H, $\mathrm{CH_2CH_2CH_2CH_2CH_2C}\mathit{H}_3$, $\mathrm{CH_2CH_2CH_2C}\mathit{H}_3$), 1.01 (m, 12H, $\mathrm{CH_2C}\mathit{H}_3$), 1.10 (t, $^3J=7.46$ Hz, 12H, $\mathrm{CH_2C}\mathit{H}_3$), 1.29, 1.40, 1.47, 1.57, 1.79, 1.98 (m, 14H, $\mathrm{CH_2C}\mathit{H}_2\mathrm{C}\mathit{H}_2\mathrm{CH_3}$, $\mathrm{CH_2C}\mathit{H}_2\mathrm{CH_2CN}$, $\mathrm{CH_2C}\mathit{H}_2\mathrm{C}\mathit{H}_2\mathrm{C}\mathit{H}_2\mathrm{C}\mathit{H}_2\mathrm{CH_3}$), 2.28 (m, 8H, $\mathrm{C}\mathit{H}_2\mathrm{CH_3}$), 2.42–2.58, (m, 10H, $\mathrm{CH_2CH_2C}\mathit{H}_2\mathrm{CN}$, $4\times\mathrm{C}\mathit{H}_2\mathrm{CH_3}$), 2.93 (m, 4H, $\mathrm{C}\mathit{H}_2\mathrm{CH_2CH_2CN}$, $\mathrm{C}\mathit{H}_2\mathrm{CH_2CH_2CH_2CH_2CH_3}$), 3.04 (m, 2H, $\mathrm{C}\mathit{H}_2\mathrm{CH_2CH_2CH_3}$), 3.78 (t, $^3J=6.75$ Hz, 1H, 20-*H*), 3.80 (t, $^3J=6.75$ Hz, 1H, 10-*H*), 6.58 (s, 1H, 15-*H*); ^{13}C NMR (125 MHz, $\mathrm{CDCl_3}$): 15.55, 15.62 (10^6-,20^6-C),17.35, 17.52 (2^2-,3^2-,7^2-,8^2-,12^2-,13^2-,17^2-,18^2-C), 18.05 (2^1-,3^1-,7^1-,8^1-,12^1-,13^1-,17^1-,18^1-C), 22.01, 24.10, 25.78, 28.23, 30.31, 32.10 (10^1-, 10^2-, 10^3-, 10^4-, 10^5-, 20^1-, 20^2, 20^3-C, 5-$\mathrm{C_{butyl}}$), 37.99 (5-,15-C), 41.12 (5-$\mathrm{C_{butyl}}$), 126.09 (10^2-,20^2-C), 127.05 (10^3-,20^3-C), 122.48 (10-,20-C) 127.07, 128.02, 130.06, 134.01, 134.13, (α-C, β-C, 20^4-C), 142.79, 144.34 (5-,15-C), 146.06 (β-C), 159.83 (α-C). UV/Vis ($\mathrm{CH_2Cl_2}$): $\lambda_{\max}$ ($\log\epsilon$)=444 nm (4.75), 551 nm (4.31); MS (EI, 80 eV): *m/z* (%): 799 (100) [$\mathrm{M^+}$], 731 (74) [$\mathrm{M^+-C_4H_6N}$], 714 (93) [$\mathrm{M^+-C_6H_{13}}$], 646 (52) [$\mathrm{M^+-C_6H_{13}-C_4H_6N}$], 603 (16) [$\mathrm{M^+-C_6H_{13}-C_4H_6N-C_3H_7}$], 590 (11) [$\mathrm{M^+-C_6H_{13}-C_4H_6N-C_3H_7-CH_3}$], 400 (17) [$\mathrm{M^{++}}$]; HRMS [$\mathrm{C_{50}H_{71}N_5Ni}$]: calcd 799.5063, found 799.5067.

3.2.10. (5-Butyl-2,3,7,8,12,13,17,18-octaethyl-15-hexyl-5,15-dihydro-10,20-diphenylporphyrinato)nickel(II) (18). A solution of 100 mg **16** (0.13 mmol) in 50 ml THF was mixed with 0.15 ml (0.3 mmol) *n*-BuLi. After 5 min the solution was treated with 1 ml *n*-hexyl iodide (0.64 mmol) and stirred for 12 h. Final purification was achieved via column chromatography on alumina using dichloromethane/*n*-hexane (1:8, v/v) as eluent. On TLC a trace of undecasubstituted porphyrin was observed. The major red band was identified as the product **18** and gave 94 mg of black crystals (0.11 mmol, 82%). Mp 183°C; ^{1}H NMR (500 MHz, $\mathrm{CDCl_3}$, TMS): $\delta=0.60$ (t, $^3J=7.5$ Hz, 12H, $\mathrm{CH_2C}\mathit{H}_3$), 1.01 (t, $^3J=7.5$ Hz, 12H, $\mathrm{CH_2C}\mathit{H}_3$), 0.94, 1.05 (each t, $^3J=7.5$ Hz, 6H, $\mathrm{CH_2CH_2CH_2CH_2CH_2C}\mathit{H}_3$, $\mathrm{CH_2CH_2CH_2C}\mathit{H}_3$), 1.33, 1.51 (m, 12H, $\mathrm{CH_2C}\mathit{H}_2\mathrm{C}\mathit{H}_2\mathrm{CH_3}$, $\mathrm{CH_2C}\mathit{H}_2\mathrm{C}\mathit{H}_2\mathrm{C}\mathit{H}_2\mathrm{C}\mathit{H}_2\mathrm{CH_3}$), 1.63 (m, 8H, $\mathrm{C}\mathit{H}_2\mathrm{CH_3}$), 2.22 (m, 8H, $\mathrm{C}\mathit{H}_2\mathrm{CH_3}$), 3.40 (m, 4H, $\mathrm{C}\mathit{H}_2\mathrm{CH_2CH_2CH_3}$, $\mathrm{C}\mathit{H}_2\mathrm{CH_2CH_2CH_2CH_2CH_3}$), 3.79 (m, 2H, 10, 20-*H*), 7.34, 7.41 (each m, 8H, $\mathrm{H_{Ph}}$), 7.63 (m, 2H, $\mathrm{H_{Ph}}$); UV/Vis ($\mathrm{CH_2Cl_2}$): $\lambda_{\max}$ ($\log\epsilon$)=444 nm (4.60), 551 nm (4.11); MS (EI, 80 eV): *m/z* (%): 884 (100) [$\mathrm{M^+}$], 827 (30) [$\mathrm{M^+-C_4H_9}$], 799 (37) [$\mathrm{M^+-C_6H_{13}}$], 741 (34) [$\mathrm{M^+-C_4H_9-C_6H_{13}}$], 442 (14) [$\mathrm{M^{++}}$]; HRMS [$\mathrm{C_{58}H_{74}N_4Ni}$]: calcd 884.5268, found 884.5266. [$\mathrm{C_{58}H_{74}N_4Ni}$, 884.53 g mol^{-1}]: Anal. calcd C 78.69, H 8.43, N 6.33, found C 78.58, H 8.14, N 6.41.

3.2.11. {5-Butyl-15-(4-ethoxycarbonylbutyl)-2,3,7,8,12,13,17,18-octaethyl-5,15-dihydro-10,20-diphenylporphyrinato}nickel(II) (19). To a solution of 100 mg **16** (0.13 mmol) in 50 ml THF 0.5 ml *n*-BuLi was added. After 3 min the solution was treated with 0.15 ml ethyl 5-iodovalerate (1.15 mmol) and stirred for 85 min. Final purification was achieved via column chromatography on alumina using dichloromethane/*n*-hexane (1:10, v/v) as eluent. The second red-brown band was identified as (5-butyl-2,3,7,8,12,13,17,18-octaethyl-10,20-diphenylporphyrinato)nickel(II) and gave 19 mg (0.02 mmol, 15%) of purple crystals.[10] The first red band gave **19** as black crystals (93 mg, 0.10 mmol, 78%). Mp 188°C; ^{1}H NMR (500 MHz, $\mathrm{CDCl_3}$, TMS): $\delta=0.50$ (t, $^3J=7.28$ Hz, 12H, $\mathrm{CH_2C}\mathit{H}_3$), 0.87 (m, 12H, $\mathrm{CH_2C}\mathit{H}_3$), 0.92 (t, $^3J=7.29$ Hz, 3H, $\mathrm{CH_2CH_2CH_2C}\mathit{H}_3$), 1.17 (t, $^3J=7.16$ Hz, 3H, $\mathrm{CH_2CH_2CH_2CH_2CO_2CH_2C}\mathit{H}_3$), 1.20–1.50, 1.82 (m, 6H, m, 2H, $\mathrm{CH_2C}\mathit{H}_2\mathrm{C}\mathit{H}_2\mathrm{CH_3}$, $\mathrm{CH_2C}\mathit{H}_2\mathrm{C}\mathit{H}_2\mathrm{CH_2CO_2CH_2CH_3}$), 1.52 (m, 8H, $\mathrm{C}\mathit{H}_2\mathrm{CH_3}$), 2.10 (m, 8H, $\mathrm{C}\mathit{H}_2\mathrm{CH_3}$), 2.36 (t, $^3J=7.40$ Hz, 3H, $\mathrm{CH_2CH_2CH_2C}\mathit{H}_2\mathrm{CO_2CH_2CH_3}$), 3.30 (m, 4H, $\mathrm{C}\mathit{H}_2\mathrm{CH_2CH_2CH_2CO_2CH_2CH_3}$, $\mathrm{C}\mathit{H}_2\mathrm{CH_2CH_2CH_2CH_2CH_3}$), 3.66 (m, 2H, 5,15-*H*), 4.05 (q, $^3J=7.16$ Hz, 2H, $\mathrm{CO_2C}\mathit{H}_2\mathrm{CH_3}$), 7.24 (m, 4H, $\mathrm{H_{Ph}}$), 7.32 (m, 4H, $\mathrm{H_{Ph}}$), 7.52 (m, 2H, $\mathrm{H_{Ph}}$); UV/Vis ($\mathrm{CH_2Cl_2}$): $\lambda_{\max}$ ($\log\epsilon$)=446 nm (4.69), 556 nm (4.13); MS (EI, 80 eV): *m/z* (%): 928 (100) [$\mathrm{M^+}$], 871 (28) [$\mathrm{M^+-C_4H_9}$], 799 (34) [$\mathrm{M^+-C_7H_{13}O_2}$], 742 (35) [$\mathrm{M^+-C_7H_{13}O_2-C_4H_9}$], 464 (20) [$\mathrm{M^{++}}$]; HRMS [$\mathrm{C_{59}H_{64}N_4O_2Ni}$]: calcd 928.5165, found 928.5184.

3.2.12. (2,3,7,8,12,13,17,18-Octaethyl-5-hexyl-10,20-diphenylporphyrinato)nickel(II) (22). Obtained as side product in the synthesis of **24**, see below. Recrystallization from CH_2Cl_2/methanol gave 19 mg (0.023 mmol, 18%) purple crystals. Mp 265°C; ^1H NMR (500 MHz, $CDCl_3$, TMS): $\delta=0.61$ (t, $^3J=7.26$ Hz, 6H, CH_2CH_3), 0.63 (t, $^3J=6.77$ Hz, 3H, $CH_2CH_2CH_2CH_2CH_2CH_3$), 0.75 (t, $^3J=7.46$ Hz, 6H, CH_2CH_3), 1.01 (m, 4H, $CH_2CH_2CH_2CH_2$-CH_2CH_3), 1.19 (m, 4H, $CH_2CH_2CH_2CH_2CH_2CH_3$), 1.52 (t, 6H, $^3J=7.54$ Hz, CH_2CH_3), 1.57 (t, 6H, $^3J=7.37$ Hz, CH_2CH_3), 3.45, 2.39 (each m, 16H, CH_2CH_3), 4.02 (m, 2H, $CH_2CH_2CH_2CH_2CH_2CH_3$), 7.46 (t, $^3J=7.46$ Hz, 4H, H_{Ph}), 7.57 (m, 2H, H_{Ph}), 8.01 (m, br., 4H, H_{Ph}), 8.99 (s, 1H, 20-*H*); UV/Vis (CH_2Cl_2): λ_{max} (log ϵ)=426 (4.89), 545 (3.88), 594 nm (3.86); MS (EI, 80 eV); *m/z* (%): 826 (100) [M^+], 751 (58) [$M^+-C_4H_9$], 413 (5) [M^{++}]; HRMS [$C_{54}H_{64}N_4Ni$]: calcd. 826.4438; found 826.4484.

3.2.13. (2,3,7,8,12,13,17,18-Octaethyl-5-hexyl-15-phenylporphyrinato)nickel(II) (23). 100 mg (0.13 mmol) of the porphodimethene **12** was dissolved in 35 ml DMF and treated with 1 ml DBU (6 mmol). The reaction mixture was heated for 30 min to 120°C. After addition of 15 ml of a 0.06 M DDQ stock solution the mixture was stirred for 50 min until TLC showed completion of the reaction. To remove polar compounds the solution was run through a short alumina column (grade III). After adding 50 ml dichloromethane, the reaction mixture was washed exhaustively with a saturated solution of $MgSO_4$ and water. The organic layer was dried over $MgSO_4$ and the final purification was achieved via column chromatography on alumina using dichloromethane/hexane (1:8, v/v) as eluent. Numerous blue, polar bands were observed as side products. Only the first-red brown fraction was collected, yielding 8 mg of **23** (0.009 mmol, 5%) as purple crystals. Mp 258°C; ^1H NMR (500 MHz, $CDCl_3$, TMS): $\delta=0.48$ (t, 3H, $CH_2CH_2CH_2CH_2CH_2CH_3$), 0.78 (m, br., 8H, CH_2CH_2-$CH_2CH_2CH_2CH_3$), 0.90 (t, 6H, $^3J=7.5$ Hz, CH_2CH_3), 1.65 (m, 12H, CH_2CH_3), 1.83 (t, 6H, $^3J=7.5$ Hz, CH_2CH_3), 2,63 (m, 4H, CH_2CH_3), 3.49–3.82 (m, 12H, CH_2CH_3), 4.30 (m, 2H, $CH_2CH_2CH_2CH_2CH_2CH_3$), 7.38–7.71 (m, 5H, H_{Ph}), 9.19 (s, 2H, 10,20-*H*), UV/Vis (CH_2Cl_2): λ_{max}(log ϵ)= 418 nm (5.18), 548 nm (3.99), 582 nm (3.81). MS (EI, 80 eV): *m/z* (%): 750 (100) [M^+], 375 (6) [M^{++}]; HRMS [$C_{48}H_{60}N_4Ni$]: calcd. 750.4138 found 750,4171.

3.2.14. (2,3,7,8,12,13,17,18-Octaethyl-5,15-dihexyl-5,15-dihydro-10,20-diphenylporphyrinato)nickel(II) (24). A solution of 100 mg (0.13 mmol) of **16** in 50 ml THF was cooled to −60°C and treated with 1.5 mmol *n*-hexyllithium. The reaction mixture was immediately oxidized without hydrolysis with 9 ml of the (0.06 mol) DDQ stock solution. Purification of the nonpolar porphodimethene fraction required an alumina column eluting with hexane. The dodecasubstituted porphodimethene **24** was obtained as black crystals (89 mg, 0.098 mmol, 57%). The second brown band was identified as the undecasubstituted porphyrin **22** (18% yield, analytical data see above); when the reaction was performed at room temperature similar results were obtained (65% **24**, 12% **22**). Mp 186°C; ^1H NMR (500 MHz, $CDCl_3$, TMS): $\delta=0.60$ (t, $^3J=7.17$ Hz, 12H, CH_2CH_3), 0.98 (t, $^3J=7.46$ Hz, 12H, CH_2CH_3), 1.05 (t, $^3J=6.93$ Hz, 6H, $CH_2CH_2CH_2CH_2CH_2CH_3$), 1.30–1.60 (m, 24H, CH_2CH_3, $CH_2CH_2CH_2CH_2CH_2CH_3$), 2.21 (m, 8H, CH_2CH_3), 3.40 (m, 4H, $CH_2CH_2CH_2CH_2CH_2CH_3$), 3.78 (m, 2H, 5,15-*H*), 7.36 (m, 4H, H_{Ph}), 7.42 (m, 4H, H_{Ph}), 7.63 (m, 2H, H_{Ph}); ^{13}C NMR (125 MHz, $CDCl_3$): $\delta=14.08$ (5^6,15^6-C), 16.01, 16.09 (3^2,7^2,13^2,17^2, 2^2,8^2,12^2,18^2-C), 17.07, 19.05 (3^1,71^2,13^1,17^1,2^1,8^1,12^1,18^1-C), 21.03 (5^5,15^5-C), 29.08 (5^4,15^4-C), 32.04 (5^3,15^3-C), 37.03 (5^2,15^2-C), 38.00 (5,15-C), 42.04 (5^1,15^1-C), 126.09 (10^2-,20^2-C), 127.05 (10^3-,20^3-C), 127.08 (10^1-,20^1-C), 129.06 (10^4-,20^4-C), 129.09 (10^2-,20^2-C), 131.00 (1,9,11,19-C), 136.05, 140.04 (10,20-C), 130.02, 143.06 (2,8,12,18,3,7,13,17-C),156.03 (4,6,14,16-C). (UV/Vis (CH_2Cl_2): λ_{max} (log ϵ)=446 nm (4.66), 559 nm (4.10); MS (EI, 80 eV): *m/z* (%): 912 (100) [M^+], 827 (81) [$M^+-C_4H_9$], 742 (38) [$M^+-C_6H_{13}$], 456 (15) [M^{++}]; HRMS [$C_{60}H_{78}N_4Ni$]: calcd 912.5576, found 912.5580; [$C_{60}H_{78}N_4Ni$, 912.56 g mol^{-1}]: anal. calcd C 78.90, H 8.61, N 6.14, found C 78.45, H 8.50, N 5.94.

3.2.15. (5-Butyl-5,15,15′-trimethyl-10,20-diphenylporphyrinato)nickel(II) (26). A Schlenk flask was charged with 0.1 mmol of **25** (50 mg) dissolved in 30 ml THF under an argon atmosphere and the solution was cooled to −70°C. Within 15 min, *n*-BuLi (0.6 mmol, 0.3 ml of a 2 M solution in cyclohexane) was added dropwise. After removal of the cold bath, the reaction mixture was stirred for 15 min and 0.5 ml water in 5 ml THF was added. After 10 min 20 equiv. of methyl iodide (0.15 ml, 2 mmol) were added. The reaction mixture was stirred for 60 min at room temperature under argon. Finally, the mixture was filtered through neutral alumina and subjected to column chromatography on neutral alumina (grade III) with ethyl acetate/*n*-hexane (1:100, v/v); yield 46 mg of **26** (82%) as deep red crystals. Mp 225°C; ^1H NMR (500 MHz; $CDCl_3$: $SiMe_4$): $\delta=1.15$ (t, $^3J=7.5$ Hz, 3H, $CH_2CH_2CH_2CH_3$), 1.35–1.50 (m, 2H, $CH_2CH_2CH_2CH_3$), 1.50–1.60 (m, 2H, CH_2CH_2 CH_2CH_3), 1.65 (s, 6H, 2×CH_3), 2.75 (s, 3H, CH_3), 3.40 (t, $J=7.5$ Hz, 2H, $CH_2CH_2CH_2CH_3$), 6.20, 6.45 (each d, $J=5.0$ Hz, 8H, 2×4$H_{\beta\text{-pyrrole}}$), 7.45–7.60 (m, 10H, H_{Ph}); ^{13}C NMR δ (500 MHz; $CDCl_3$: $SiMe_4$): $\delta=14.15$, 23.33, 27.75, 37.94, 38.92, 42.70, 51.25, 113.68, 115.11, 127.33, 128.39, 130.32, 131.09, 131.28, 135.28, 136.35, 136.86, 166.15, 166.28; UV/Vis (CH_2Cl_2): λ_{max}(log ϵ)=432 (4.62), 532 (4.12); MS (EI, 80 eV): *m/z* (%): 618 (21) (M^+), 603 (9) [M^+-CH_3], 588 (4) [$M^+-2\times CH_3$], 561 (85) [$M^+-C_4H_9$], 546 (100) [$M^+-C_4H_9-CH_3$], 531 (8) [$M^+-C_4H_9-2CH_3$], 309 (3) [M^{++}]. HRMS [$C_{39}H_{36}N_4Ni$]: calcd 618.2296, found 618.2293.

3.2.16. (5-Butyl-5,15,15′-tricyanomethyl-10,20-diphenylporphyrinato)nickel (II) (27). Synthesis followed the procedure given for **26**. Chromatography of the reaction mixture eluting with ethyl acetate/*n*-hexane (5:1, v/v); gave 51 mg of **27** (78%) as deep red crystals (CH_2Cl_2/CH_3OH). Mp 252°C; ^1H NMR (500 MHz; $CDCl_3$: $SiMe_4$):$\delta=1.20$ (t, $^3J=7.5$ Hz, 3H, $CH_2CH_2CH_2CH_3$), 1.35–1.45 (m, 2H, $CH_2CH_2CH_2CH_3$), 1.50–1.65 (m, 2H, $CH_2CH_2CH_2CH_3$), 3.0, 3.25 (each s, 4H, 2×CH_2CN), 3.45 (m, 2H, $CH_2CH_2CH_2CH_3$), 4.75 (s, 2H, CH_2CN), 6.20 (m, 4H, 4$H_{\beta\text{-pyrrole}}$), 6.45, 6.55 (each d, 4H, $J=5.0$ Hz, 2×2$H_{\beta\text{-pyrrole}}$), 7.45–7.60 (m, 10H, H_{Ph}); ^{13}C NMR (500 MHz; $CDCl_3$: $SiMe_4$): $\delta=13.95$, 23.11, 23.47, 27.26, 35.39, 43.09, 45.84, 49.44, 114.19, 115.82, 116.13, 116.31, 117.31, 127.64, 129.21, 130.22, 132.03, 133.94, 135.64, 137.06, 137.34, 146.62, 156.11, 162.33; UV/Vis (CH_2Cl_2):

λ_{max}(log ϵ)=430 (4.72), 535 (4.15); MS (EI, 80 eV): *m/z* (%): 693 (22) [M^+], 652 (75) [M^+-CH_2CN], 612 (100) [$M^+-2\times CH_2CN$], 515 (41) [$M^+-C_4H_9-CH_3$]. HRMS [$C_{42}H_{33}N_7Ni$]: calcd 693.2151, found 693.2172.

3.2.17. {5-Butyl-5,15,15′-tri(3-cyanopropyl)-10,20-diphenylporphyrinato}nickel (II) (28). A Schlenk flask was charged with 0.1 mmol of the (5,15-diphenylporphyrinato)nickel (II) **25** (50 mg) dissolved in 30 ml THF under an argon atmosphere and the solution was cooled to −70°C. Within 15 min, *n*-BuLi (0.6 mmol, 0.3 ml of a 2 M solution in cyclohexane) was added dropwise. After removal of the cold bath, the reaction mixture was stirred for 15 min and 0.5 ml water in 5 ml THF was added. After 10 min 40 equiv. of the 3-cyanopropyl iodide (0.3 ml) were added. The reaction mixture was stirred for 60 min at room temperature under argon and then heated at 50°C for another 60 min. Finally, the mixture was filtered through neutral alumina and subjected to column chromatography on neutral alumna (grade III) with dichloromethane/acetone (100:1, v/v); yield 31 mg of **28** (40%) as deep red crystals (dichloromethane/*n*-hexane). Mp 217°C; ^1H NMR (270 MHz; $CDCl_3$: $SiMe_4$): δ=1.05 (t, ^3J=7.5 Hz, 3H, $CH_2CH_2CH_2C\mathit{H}_3$), 1.35–1.50 (m, 6H, $CH_2CH_2C\mathit{H}_2CH_3$, $2\times CH_2C\mathit{H}_2CH_2CN$), 1.70–2.00 (m, 8H, $CH_2C\mathit{H}_2CH_2CH_3$, $2\times C\mathit{H}_2CH_2CH_2CN$, $CH_2C\mathit{H}_2$-CH_2CN), 2.45–2.65 (m, 6H, $CH_2CH_2C\mathit{H}_2CN$), 2.75–3.50 (m, 4H, $C\mathit{H}_2CH_2CH_2CH_3$, $C\mathit{H}_2CH_2CH_2CN$), 6.20 (m, 4H, $4\times H_{\beta\text{-pyrrole}}$), 6.45, 6.50 (each d, *J*=5.0 Hz, 4H, $2\times 2H_{\beta\text{-pyrrole}}$), 7.45–7.60 (m, 10H, H_{Ph}); UV/Vis (CH_2Cl_2): λ_{max}(log ϵ)=436 (4.58), 537 (4.19); MS (EI, 80 eV): *m/z* (%): 777 (22) [M^+], 720 (36) [$M^+-C_4H_9$], 709 (100) [$M^+-CH_2CH_2CH_2CN$], 652 (34) [$M^+-C_4H_9-CH_2CH_2$-CH_2CN], 641 (31) [$M^+-2\times CH_2CH_2CH_2CN$], 598 (18) [$M^+-C_4H_9-CH_2CH_2CH_2CN-CH_2CH_2CN$], 587 (6) [$M^+-2\times CH_2CH_2CH_2CN-CH_2CH_2CN$], 544 (16) [$M^+-2\times CH_2CH_2CH_2CN-CH_2CH_2CN-CH_2CH_2CH_3$]. HRMS-[$C_{48}H_{45}N_7Ni$]: calcd 777.3090, found 777.3054.

3.3. Crystal structure determination of 7

The crystals were immersed in hydrocarbon oil (Paraton N®), a single crystal selected, mounted on a glass fiber and placed in the low-temperature N_2 stream.[19] Intensity data were collected at 85 K with a Bruker SMART system complete with 3-circle goniometer and CCD detector utilizing MoK_α radiation (λ=0.71073 Å). The intensities were corrected for Lorentz and polarization effects. An absorption corrections was applied using the program SADABS,[20] extinction effects were disregarded. The structure was solved with Direct Methods using the SHELXTL PLUS program system[21a] and refined against $|F^2|$ with the program XL-97 using all data.[21b] Nonhydrogen atoms were refined with anisotropic thermal parameters. Hydrogen atoms were generally placed into geometrically calculated positions and refined using a ridging model.[22]

3.4. Crystal data for 7

$C_{44}H_{62}N_4Ni$. F_W=705.69, red block from CH_2Cl_2/CH_3OH, crystal size 0.3×0.25×0.21 mm, monoclinic, $P2_1/n$, a= 14.9471(7) Å, b=18.5337(10) Å, c=15.0197(7) Å, β= 112.840(1)°, V=3834.6(3) Å^3, Z=4, d_{calcd}=1.222 Mg m^{-3}, $\mu(MoK_\alpha)$=0.542 mm^{-1}, T_{min}=0.854, T_{max}=0.895, θ_{max}= 31.52°, 12103 independent reflections, R_{int}=0.078, 7930 reflections with $I>2.0\sigma(I)$, 453 parameters, $R1$ ($I>2.0\sigma(I)$)=0.0603, $R1$ (all data)=0.1047, $wR2$ (all data)=0.1551, S=1.036, ρ_{max}=1.704e Å^{-3}.

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