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Alkylation of the Inverted Porphyrin Nickel(II) Complex by Dihalogenalkanes: Formation of Monomeric and Dimeric Derivatives

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An efficient and simple method of modification of "inverted" porphyrin is provided by reactions of 5,10,15,20-tetraaryl-2-aza-21-carbaporphyrinatonickel(II) **2** with dihalogenalkanes under basic conditions. The substituents are bound to the internal carbon or external nitrogen of the inverted pyrrole depending on dihalogenalkane and basic catalyst. The monomeric 2- or 21-ethoxymethyl-substituted species are formed in the reaction of **2** with dihalomethanes and sodium ethoxide or ethanol in the presence of K_2CO_3. A novel, dimeric 21,21′-ethylene-linked derivative **11** is obtained from **2** and ethylene bromide in dichloromethane in the presence of potassium carbonate end ethanol, while application of potassium *tert*-butoxide promotes formation of *N*-bromoethyl-substituted monomer **12**. Reaction of **2** with propylene bromide in the presence of proton scavenger efficiently leads to the 21-allyl-substituted monomer **14** that is a product of the HBr elimination from a transient 21-bromopropyl-substituted species. The new compounds have been identified and characterized by means of mass spectrometry and optical and NMR spectroscopies. A single-crystal X-ray analysis performed for **12** allows discussion of structural parameters concerning the macrocycle and coordination core. Formation of deprotonated species $[\mathbf{2}]^-$, which is proposed as a key intermediate in the alkylation reaction, has been observed spectroscopically. Chirality of the N-substituted derivatives induced by protonation of the internal carbon is observed by NMR at low temperatures.

Introduction

"Inverted" or "N-confused" porphyrin is an isomer of the regular porphyrin in which the positions of nitrogen and carbon atom are interchanged in one of the pyrrole units. Discovery of the *meso*-tetraaryl-substituted inverted porphyrin **1** among the products of the Rothemund condensation[1,2] and its subsequent optimization[3] with respect to **1** make this aromatic tetrapyrrolic macrocycle a readily obtainable and therefore attractive subject of studies and modification.

Without changing the macrocyclic skeleton, inverted porphyrin offers profound alteration of the optical and coordination properties with respect to those of regular porphyrins. That brings a potential for creation of novel organic and inorganic compounds and materials with building blocks structurally analogous to the well-known tetrapyrroles.

The reactivity of the inverted pyrrole may be beneficial for the efforts aimed at the programmed modification of the macrocycle. In fact, most of the modifications introduced to date to the inverted porphyrin have been located on this fragment.[4]

A unique property of the inverted porphyrin is its ability to form organometallic complexes[1,5,6] **2**−**5**, in which the external nitrogen of the inverted pyrrole is a potential target of coordination or hydrogen bonding. Coordination through the deprotonated internal carbon of the inverted pyrrole, such as that observed in the nickel(II) complex **2** or **3**, activates 21-C, making it the primary target of an electrophilic attack.[5b,7,8]

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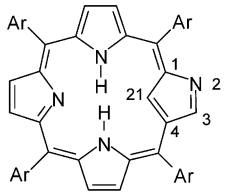
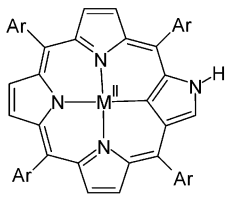
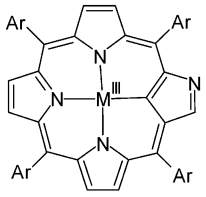


1: Ar = Ph
1a: Ar = *p*-Tol



2: M = Ni^{2+}
3: M = Cu^{2+}
4: M = Pd^{2+}



5: M = Ag^{3+}

In the present paper we report on the synthesis and characterization of a series of compounds—the products of reaction of **2** with dihalogenalkanes. These readily available bis-electrophiles are expected to react with inverted pyrrole, yielding covalently linked bis(carbaporphyrinoids). Otherwise, a reaction of the "free end" of the halogenalkyl bound to the inverted pyrrole with nucleophiles present in the reaction mixture should give products that extend the class of modified carbaporphyrinoids (Scheme 1).

The set of possible products extends on those in which the external nitrogen of the inverted pyrrole is involved in alkylation as a target of electrophilic attack. Thus, formation of *N*-halogenalkylated monomers and *C*,*N*′- or *N*,*N*′-alkylene-linked dimers,[8] as well as a variety of 2,21-bis-substituted monomeric[7,9] and dimeric complexes, can be anticipated if reaction conditions promote deprotonation of the external nitrogen, enhancing its nucleophilic character. Having this in mind, we also focus on the parameters that allow reaction selectivity control.

Results and Discussion

Syntheses and Characterization. The general synthetic protocol involves mixing a dichloromethane solution of **2** with an excess of the appropriate dihaloalkane in the presence of a proton scavenger. Reaction progress can be monitored by UV—vis and ^{1}H NMR spectroscopies. Products of the reaction are separated chromatographically and characterized by mass spectrometry, optical spectra, and ^{1}H and ^{13}C NMR, including 2D homo- and heteronuclear correlation techniques.

In dichloromethane solution, **2** seems to be stable, even at elevated temperature in the absence of air or base. However, CH_2Cl_2 becomes a moderately effective bifunctional alkylating agent toward **2** under basic conditions. Addition of sodium ethoxide to the solution of **2** in CH_2Cl_2 under anaerobic conditions resulted in its conversion into the 21-ethoxymethyl derivative **6** (Scheme 2). The same product can be obtained using an alcoholic NaOH solution or a suspension of K_2CO_3 in alcohol; however, the conversion is slower. A certain portion (up to 10%) of **2** is converted to its 2-ethoxymethyl-substituted derivative **7** as a minor product, in addition to the internally substituted **6**. Product **7** dominates when the reaction is carried out using CH_2Br_2/EtOH/K_2CO_3/dibenzo[18]crown-6 system in refluxing dichloromethane. Formation of bis(carbaporphyrinoids) **8** (major product) and **9** reported by us recently[8] is not observed when the reaction of **2** with dihalomethane is carried out in the presence of a primary or secondary alcohol in the reaction mixture; the alkoxymethyl derivatives such as **6** are formed instead. On the other hand, slow formation of only **8** (major product) and **9** is observed upon addition of an excess of potassium *tert*-butoxide in THF to the solution of **2** in dichloromethane under dry anaerobic conditions (see the Experimental Section for details).

Optical spectra of **6** or **7** (Figure 1) resemble those of 21- or 2-methylated derivatives, respectively.[4a,7] The spectrum of **7** is also very similar to that of the starting complex **2**. The considerable difference between the spectra of the internally and externally alkylated isomers allows their facile distinction. Both spectra also significantly differ from those of dimeric **8** and **9**.[8]

The alkylation with dihalomethanes involves three components: the starting complex **2**, the CH_2-linker, and the other part of the substituent that may be either an alkoxide or another molecule of the complex. The structure of the products and the origin of the linker can be determined using ^{1}H and ^{13}C NMR.

The ^{1}H NMR characteristics of **6** are in line with its description as a diamagnetic monomeric 21-alkylated derivative of a nickel(II) complex of inverted porphyrin.[7] The spectral features include a pair of diastereotopic methylene 1′ signals (−1.29, −1.38 ppm, ^2J = 9.2 Hz). Their high-field positions are due to the shielding effect of the aromatic ring-current, indicating the intraannular location of the substituent (Figure 2A). These signals are absent in the ^{1}H NMR spectrum of **6**-d_2 (the product obtained from the reaction carried out in a CD_2Cl_2 solution), but they can be observed in the ^{2}H NMR spectrum (Figure 2C). That selective deuteration indicates dichloromethane as the source of the methylene group that is directly bound to 21-C.

The diastereotopic differentiation of these protons reflects the chirality of the molecule that is related to the asymmetry of the internal carbon of the inverted pyrrole. In fact, the chemical shift of 21-C in the ^{13}C NMR spectrum (36.5 ppm) is typical for aliphatic carbon atoms, and thus, its sp^3 hybridization can be inferred. The diastereotopic differentiation extends on the more distant parts of the substituent. The methylene signals of the ethyl group (3′-CH_2), instead of being a quartet, displays a much more complicated pattern of an ABX_3 system (Figure 2A′).

The presence of a pyramidal carbon atom in the coordination core of the macrocycle causes nonplanarity of the system, resulting in differentiation of the ortho-protons of each *meso*-phenyl ring. Due to rotation, these protons show broad signals in the region of 7.9—8.3 ppm at 298 K being in chemical exchange, but they sharpen

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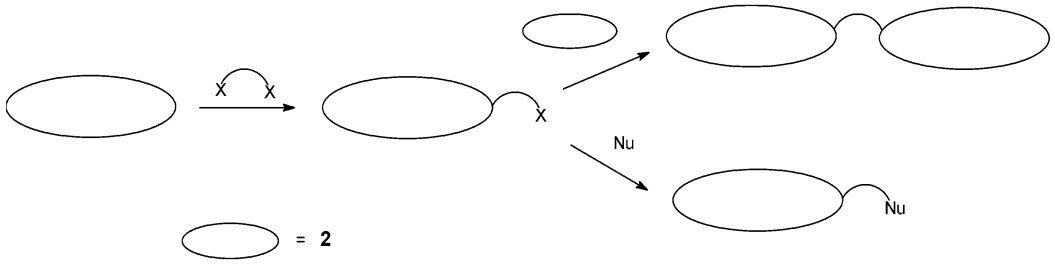
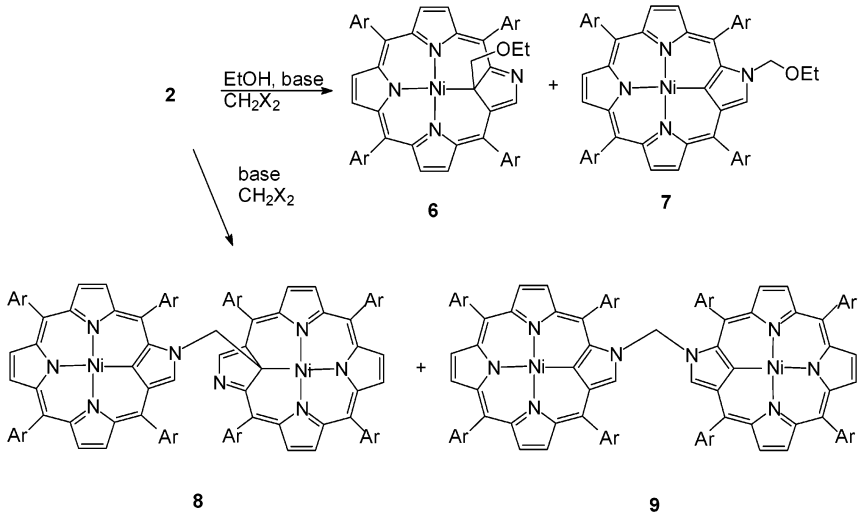
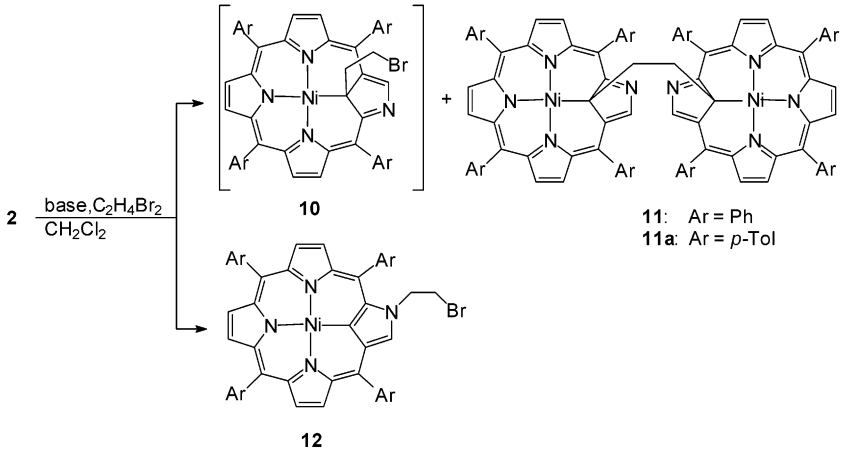
SCHEME 1. Possible Paths of Reaction of 2 with Dihaloalkanes



SCHEME 2. Reactions of 2 with Dihalomethanes



SCHEME 3. Reaction of 2 with 1,2-dibromoethane



and differentiate their chemical shifts at lower temperatures (233 K) as the rotation becomes slow on the NMR time scale.

Complex **7**, which is isomeric with **6**, possesses an effective plane of symmetry. Thus, the methylene group attached to the external nitrogen gives a singlet at about 5 ppm, and the ethyl group is represented by a quartet and triplet (Figure 1D). The low-field part of the spectrum of **7** (7.5−8.6 ppm) resembles that of the nickel(II) complex of the 2-methylated derivative of inverted porphyrin.[4a]

To some extent the ^{1}H NMR spectrum of the 2,21′-CH_2-linked, asymmetric dimer[8] unites features characteristic of the nickel complexes alkylated on the external nitrogen **7** and those of internally alkylated species such as **6**. There are, however, some significant attributes of the spectrum of **8** that are related to its dimeric structure and the aromatic character of both subunits. The effect of the closeness of the porphyrinoid rings is unequally distributed over the molecule. The significant upfield shift can be observed for some protons of the N-substituted part of the complex, particularly for the 3-proton proximal to the methylene linker and for protons of one of the *meso*-phenyls. Also in the case of a symmetric 2,2′-CH_2-linked dimer, positions of proton 3 and some of the phenyl protons in the ^{1}H NMR are high-field shifted[8] with respect to that of the monomeric *N*-methylated nickel(II) complex of inverted porphyrin.[4a]

1,2-Dibromoethane reacts with **2** (Scheme 3) in a dichloromethane/ethanol solution in the presence of a

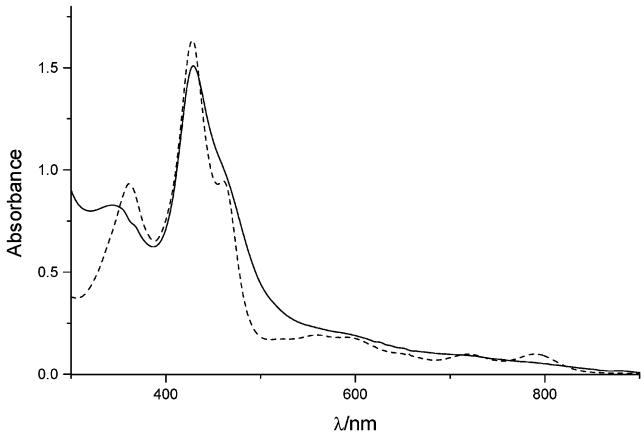


FIGURE 1. Optical spectra of **6** (solid line) and **7** (dashed line) in CH_2Cl_2.

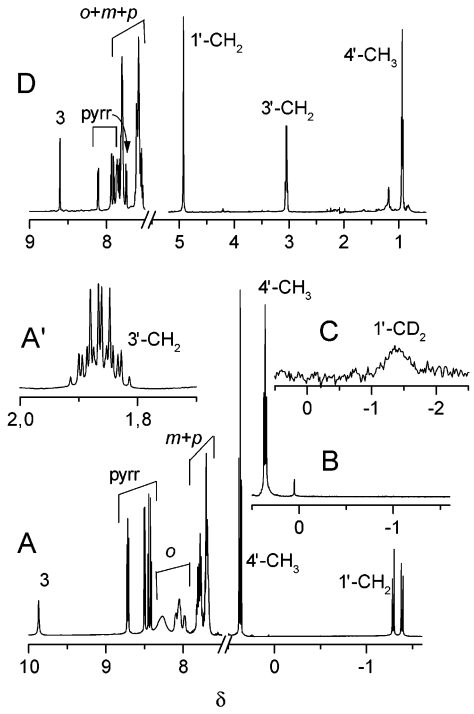


FIGURE 2. NMR spectra of **6** (A, A′, $CDCl_3$, 298 K) and **6**-d_2 (B, the high-field part of the ^{1}H NMR spectrum in $CDCl_3$; C, ^{2}H NMR, $CHCl_3$), and **7** (D, $CDCl_3$, 298 K) Assignments: pyrr, *β*-pyrrole, 3, inverted pyrrole; *o*, *m*, *p*, ortho, meta, and para protons of *meso*-aryls, respectively.

suspension of K_2CO_3, giving the 21,21′-ethylene-linked dimer **11** as the major product (up to 52%). In the reaction mixture a transient monomeric 21-bromoethyl-substituted complex **10** can be observed by ^{1}H NMR and mass spectrometry prior to reaction completion; however, our attempt to isolate this product failed. On the other hand, a considerable amount (up to 20%) of monomeric 2-bromoethyl-substituted product **12** can be isolated from the reaction mixture. The substituent in **12** seems to resist any further reactivity, even under strongly basic conditions. Neither the Williamson-type reaction of the bromoethyl-substituted products **10** or **12** with alcohol nor formation of 2,21′- or 2,2′-ethylene-linked dimers is observed in the reaction mixture. Interestingly, the

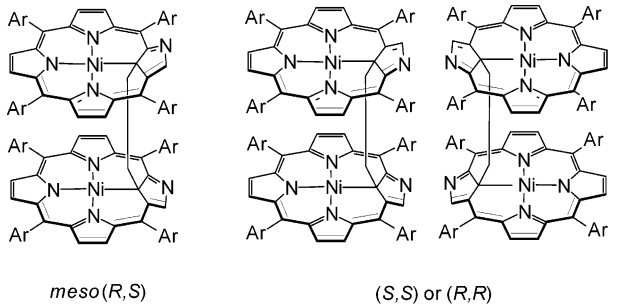


FIGURE 3. Stereoisomers of **11**.

dimeric product **11** dominates, despite the excess of dibromoethane used in the reaction. It seems that the reaction mechanism involves slow formation of **10**, followed by a relatively fast consumption of this transient species by the unsubstituted **2**.

Although reaction does not proceed without a basic catalyst, it appears that very strong bases can alter the reaction path by making the external nitrogen the primary alkylation target, likely due to deprotonation of this site (vide infra). In fact, reaction of **2** with a 10-fold excess of dibromoethane in refluxing THF solution containing 10 equiv of *t*-BuOK yields after 2 days only traces of **11** and about 70% of **12**.

To the best of our knowledge, **11** is the first example of a bis(carbaporphyrinoid) in which the coordination cores of the subunits are covalently linked in this manner. However, a related system is known for regular porphyrins. Vinylene-*N*,*N*′-linked bis-porphyrin dicobalt(II) has been observed as the final product in the transformation of the acetylene adduct of tetraphenylporphyrinatocobalt(III) perchlorate.[10]

The vicinity of two aromatic macrocycles determines the ^{1}H NMR spectral pattern of **11** and **11a**. The "symmetrical" dimer of that type contains in fact two asymmetric carbons linked by an ethylene bridge. These carbons can have the same or opposite configurations, giving either a mixture of enantiomers that are indistinguishable by NMR, or a diastereoisomeric meso form (Figure 3).

On the basis of the molecular modeling, free rotation around the bond between 21-C and the ethylene carbon can be assumed. Thus, the structure of each stereoisomer has effectively a 2-fold symmetry, causing degeneration of the ^{1}H NMR signals of the dimer. However, in the spectrum of **11** or **11a** (Figure 4), two sets of peaks are observed, which is indicative of a mixture of diastereoisomers. This is particularly well shown by the methyl signals of the *meso*-tolyl substituents of **11a**, for which eight partially overlapping peaks of equal intensity appear in the region of 2.3−2.8 ppm at 233 K, indicating the equimolar contribution of both diastereoisomers.

Protons of the ethylene linker give complicated multiplets in the region of −4.6 to −5.0 ppm. Their positions are markedly shifted upfield (about 2 ppm)[7] with respect to that of the monomeric complexes, indicating stronger shielding of the ethylene protons caused by the proximity of two aromatic porphyrinoid rings. The complexity of the signals comes from the occurrence of diastereoisomers,

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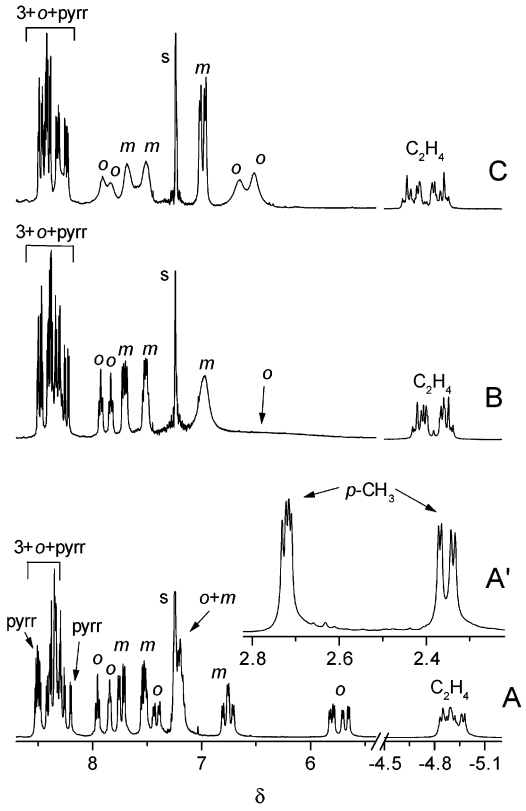
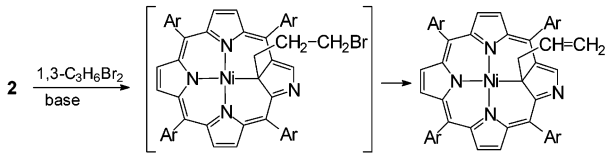


FIGURE 4. ^{1}H NMR spectra of **11a** (500 MHz, $CDCl_3$): A, A′, 233 K; B, 298 K; C, 330 K. Assignments: pyrr, β-pyrrole; 3, inverted pyrrole; *o, m*, ortho and *meta* protons of *meso*-tolyl rings, respectively; s, $CHCl_3$.

diastereotopic differentiation of the methylene protons, and their couplings. Moreover for **11** and **11a**, the ethylene signals of the diastereoisomers overlap differently at different temperatures, since their chemical shifts vary, likely due to changes in the rotation rate around the axis that is set by the ethylene linker. The signals of protons in position 3, i.e., adjacent to the external nitrogen of inverted pyrroles of both diastereoisomers, are also shifted upfield with respect to their position in the spectra of monomers (9.7 ppm),[7] appearing for **11a** in the region of 8.2−8.4 ppm. They strongly overlap with signals of β-pyrrole and *meso*-aryl protons but can be identified on the basis of the heteronuclear couplings with 21-C (37.1 ppm at 233 K) and 1-C (176.7, 177.4 ppm).

The dynamic effects can also be observed for some of the *meso*-aryl protons. At low temperatures (213−243 K), two aryl rings of each diastereoisomer give four well-resolved signals of ortho-protons that are shifted upfield (5.5−6.0 ppm). The strong NOE correlations with protons of the ethylene bridge and proton 3 allow assignment of these signals to the aryl rings that are located in meso positions adjacent to the inverted pyrrole. We have assigned a group of four other ortho-protons belonging to the same aryl rings signals of that appear in the region of 7.1−7.5 ppm. At room temperature instead of these eight signals there is only a very broad line (halfwidth about 400 Hz) at 6.5 ppm (Figure 4B) that splits into two lines at 330 K (Figure 4C). Similarly, above 243 K the eight signals of meta-protons coalesced into a broad

SCHEME 4. Reaction of 2 with Propylene Bromide



feature at about 7 ppm. They sharpen again at 330 K as four distinct peaks.

In the case of monomeric 21-substituted porphyrinoids, rotation rates of all *meso*-aryl rings are similar, as can be estimated on the basis of their similar temperatures of coalescence.[11] In **11** and **11a**, the effect of line broadening at 298 K is limited to the signals of the ortho- and meta-protons of the aryl rings that are in the neighborhood of the inverted pyrrole and the linker (i.e., bound to the porphyrin meso-carbons 5 and 20). The signals of the other aryl protons (7.5−8 ppm) remain sharp in the temperature limit 213−313 K, which indicates that their rotation is slow and does not average chemical shifts of the magnetically inequivalent protons. It implicates a significant difference in the rotational freedom of aryl rings belonging to the different part of the porphyrin subunit. Similar distinction in dynamic phenomena have been reported for vinylene-*N*,*N*′-linked diporphyrin.[10]

The electronic spectra of **11** or **11a** display a pattern typical of 21-alkylated nickel(II) complexes of inverted porphyrin, suggesting a lack of any significant interaction between the π-systems of the aromatic subunits of the dimer.

The 2-bromoethyl-substituted complex **12** displays spectral features typical of monomeric nickel complexes of inverted porphyrin. The optical spectrum resembles that of **2** or **7** differing slightly in the relative intensity of the absorption bands. Also, ^{1}H NMR is similar to that of **7** with two diagnostic triplets of the bromoethyl substituent at 4.11 (1′-CH_2) and 3.38 ppm (2′-CH_2), indicating the effective planarity of the molecule.

Reaction of **2** with 1,3-dibromopropane carried out in THF with *t*-BuOK at room temperature yields exclusively a monomeric 21-allyl-substituted product **14** (Scheme 4). Clearly, the 1,2-elimination of HBr is under these conditions a much more favorable process in comparison with dimerization. In fact, formation of **14** follows that of a transient 21-(3′-bromopropyl) derivative, **13**, which can be observed by ^{1}H NMR and mass spectrometry when the reaction is carried out in dichloromethane with a less aggressive proton scavenger, i.e., K_2CO_3/EtOH (see Supporting Information). Interestingly, no 2-N-substituted products can be observed, despite reaction conditions similar to those just described for ethylene bromide where a certain amount of **12** is always formed. The selectivity of the reaction with dibromopropane is promising for the further application of functionalized inverted porphyrin. The olefinic functionality, together with conveniently oriented external nitrogen, constitutes a potential coordination site for transition metals in low oxidation states.

The NMR spectra of **14** (Figure 5) unequivocally indicate the presence of an allyl substituent bound to

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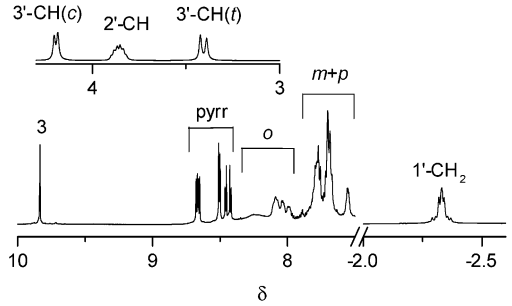


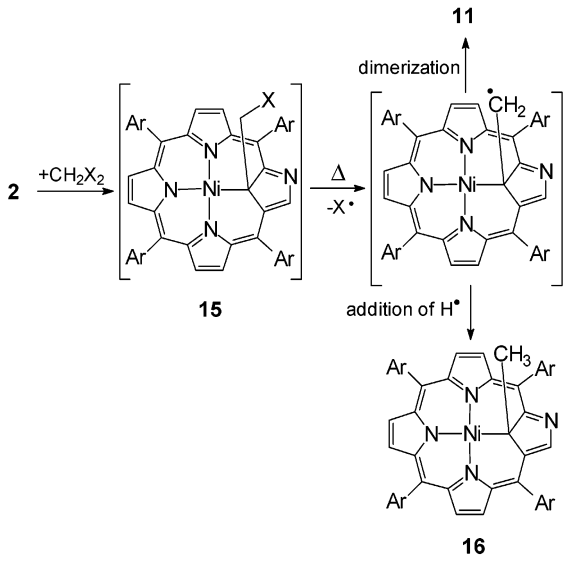
FIGURE 5. ^{1}H NMR spectrum of **14** (500 MHz, 298K, $CDCl_3$). The inset shows the extended olefinic region of the spectrum. Assignments: pyrr, *β*-pyrrole; 3, inverted pyrrole; *o*, *m*, ortho and meta protons of *meso*-phenyl rings, respectively, *c* and *t* denote respectively the cis and trans proton of the terminal methylene of the allyl substituent.

21-C showing a set of three signals in the region of 4.5−3 ppm scalar coupled to the upper-field multiplets of diastereotopic methylene protons at about −2.5 ppm. The other spectral features of **14** closely resemble those of other 21-substituted nickel complexes of inverted porphyrin,[7] including **6**.

The reactions of **2** with dihalomethanes accelerate considerably when carried out at elevated temperature. However, formation of other, rather unexpected products can be observed for the refluxed reaction mixtures. For example, a certain amount of a 21-methyl-substituted product[7] **16** (5%) and dimer **11** (10%) accompanying the formation of **6** (30%) can be observed in the reaction mixture when **2** reacts under reflux with CH_2Cl_2 and an ethanolic solution of sodium hydroxide in the presence of air. Similarly, formation of traces of both **11** and **16** is observed under strictly anaerobic conditions upon refluxing a solution of **2** with an excess of diiodomethane in CH_2Cl_2 with no basic catalyst together with unsymmetrical dimer **8** as a major product (20%). The homolitic abstraction of the halogen from a transient product **15** followed by free-radical reactions should be assumed to account for this observation, since no source of methyl or ethylene substituents is present in the system (Scheme 5). Thus, although we assume that the formation mechanism of the major products is mainly ionic, under certain conditions liberation of radicals can open alternative reaction paths. It can be related to the redox properties of the nickel center for which oxidation state +3 is relatively easily accessible in the environment of inverted porphyrin[5a] and may initiate the reaction chain. On the other hand, exclusion of atmospheric oxygen does not prevent formation of byproducts. Oxidative addition involving metal ion may be operative in this case. Such a process has been suggested previously for the methylation of **2** with methyl iodide.[7] Oxidation of the metal center followed by a free-radical process has been proposed for the inner C-arylation of a doubly N-confused porphyrin palladium(II) complex in toluene.[12]

Structural Characterization of 12. A single-crystal X-ray diffraction analysis has been performed for the complex **12** (Figure 6). There is some disorder involving bromoethyl substituent and inverted pyrrole (see Experimental Section) which, however, does not preclude identification of atoms in the macrocycle.

SCHEME 5. Proposed Mechanism of Byproduct Formation in the Reaction of 2 with Dihalomethanes



The Ni−N distances are comparable to those in the nearly planar diamagnetic (OEP)Ni^{II} complex (1.958(2) Å)[13] in the triclinic form and are consistent with the average distances 1.955(3) and 1.963(3) Å determined for the disordered nickel(II) complex of inverted *meso*-tetratolylporphyrin.[1] These distances are slightly longer than those found for the tetragonal modification of (OEP)-Ni^{II} (1.929(3) Å)[14] and two out of three Ni−N bonds in nickel(II) complex of azuliporphyrin (1.934(3) and 1.928-(3) Å).[15] All Ni−N bonds distances are similar, unlike in the latter case,[15] where the trans-effect of the more basic C(21) has been suggested as a source of slight elongation of the Ni−N(23) distance (1.964(2) Å).[15]

The Ni−C bond length 1.906(4) Å in **12** is within the limits of Ni(II)−C bond lengths (1.81−2.02 Å).[15−17] This bond is slightly longer than the corresponding bond in the constrained van Koten's nickel(II) system [(2,6-Me_2-$NCH_2)_2C_6H_3$]Ni^{II}(HCOO) (1.814(2) Å)[16] and comparable with the respective distance in the complex of azuliporphyrin (1.897(3)).[15] It is considerably shorter than the bond distance in the nickel(II) complex of 21-methylated inverted porphyrin (2.005(6) Å),[7] where the coordinated carbon adopts an sp^3 hybridization.

The structure shows a slight saddle-shaped distortion of the molecule. The coordination core is essentially planar with nickel(II) ion displaced about 0.03 Å from the N(1)−N(2)−N(3) plane. The more pronounced deviation from this plane is observed for C(21) (0.200(4) Å).

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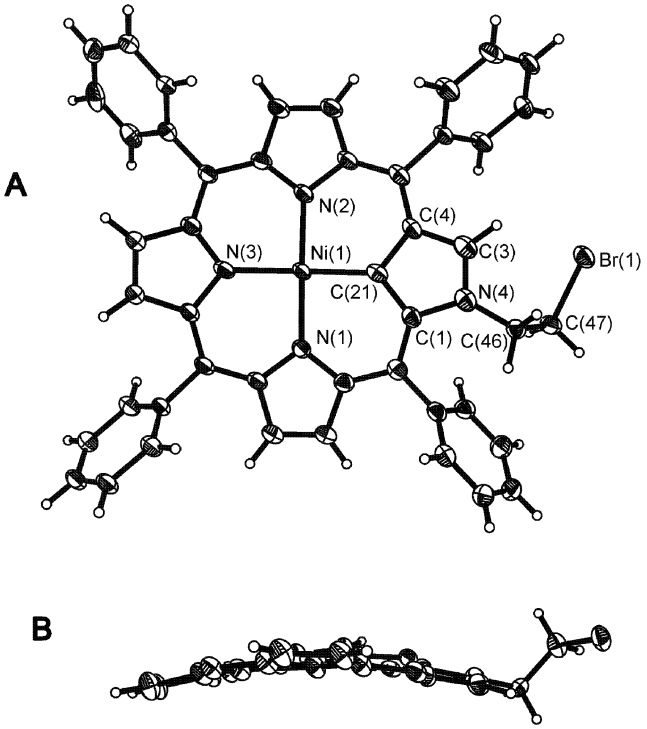


FIGURE 6. (A) ORTEP plot (50% probability) of **12** with hydrogen atoms arbitrarily drawn small. Selected bond lengths (Å) and angles (deg): Ni(1)−C(21) 1.906(4), Ni(1)−N(1) 1.959-(3), Ni(1)−N(3) 1.962(4), Ni(1)−N(2) 1.964(4), C(1)−C(21) 1.404(6), C(4)−C(21) 1.423(5), C(3)−C(4) 1.421(6), N(4)−C(1) 1.432(5), N(4)−C(3) 1.315(6), N(4)−C(46) 1.447(7), C(46)−C(47) 1.502(9), Br(1)−C(47) 1.951(6), C(21)−Ni(1)−N(1) 88.90(16), C(21)−Ni(1)−N(3) 175.78(16), N(1)−Ni(1)−N(3) 90.79(14), C(21)−Ni(1)−N(2) 90.12(16), N(1)−Ni(1)−N(2) 177.88(15), N(3)−Ni(1)−N(2) 90.33(15), C(1)−C(21)−C(4) 103.9(4), C(1)−C(21)−Ni(1) 129.3(3), C(4)−C(21)−Ni(1) 126.7(3). (B) Edge view ORTEP drawing of **12**. In this view the phenyl rings are omitted for clarity.

This is in line with the stronger displacement of the inverted pyrrole atoms (0.599(3) Å for N(4) and 0.705(2) Å for C(3)) in comparison with the β-pyrrole carbons, for which the absolute value of deviation ranges from 0.26 to 0.39 Å.

The known structures of divalent metal complexes of the inverted porphyrins with deprotonated C(21) i.e., **2**[1] and **4**,[5e] are disordered, preventing discussion of structural parameters. The unsubstituted inverted porphyrin **1** as a ligand can adopt mono-,[5b,g,h] di-,[1,5a,b,e,i,6] or trianionic[5c,d,j] character, depending on the metal ion coordinated within the porphyrin crevice. In the case of divalent nickel or palladium, the redundant negative charge is neutralized by the proton attached to the external nitrogen. A substituent bound to the external nitrogen plays the same role of fixing the dianionic character of the macrocycle in the nickel(II) complex. Thus, **12** can serve as a structural analogue of **2**, since both systems possess identical chromophore and display very similar spectral features.

Deprotonation of the Starting Material. Alkylation of **2** by dihaloalkanes proceeds effectively in the presence of proton scavengers. Clearly, basic conditions enhance the nucleophilic character of the starting complex, likely by deprotonation of the external nitrogen of the inverted

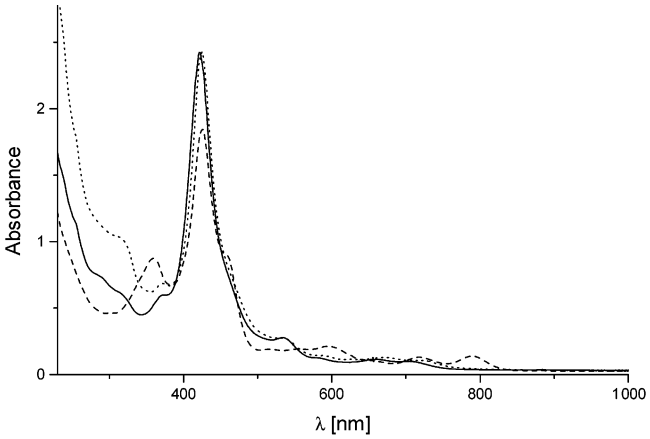


FIGURE 7. Selected optical spectra recorded in the course of titration of **2** (CH_2Cl_2 solution) with *t*-BuOK (THF solution): dashed line, starting complex **2**; solid line, after addition of 1 equiv of base; dotted line, after addition of 20 equiv of base.

pyrrole. The effective abstraction of proton from **2** can be accomplished by addition of strong bases under strictly anhydrous conditions, since the resulting deprotonated species is highly hydrolytically unstable and it turns back into **2** in the presence of moisture. The spectrophotometric titration of **2** in dichloromethane solution with potassium *tert*-butoxide reveals significant spectral changes (Figure 7), i.e., an increase of Soret band intensity and a blue-shift of Q-bands.

The ^{1}H NMR-controlled titration of **2** in CD_2Cl_2 with *t*-BuOK in THF allows observation of a gradual disappearance of a signal of 2-NH at 10 ppm[1] that is accompanied by a low-field shift of signals of β-pyrrolic protons and initial broadening of all but one spectral line, implying fast chemical exchange between protonated and deprotonated forms (Figure 8). Interestingly, the chemical shift and line width of a signal of proton 3 that is the closest neighbor of the external nitrogen remains almost unchanged up to the point in which the 2-NH signal disappears completely (1.2 equiv of base). It implies the similar values of chemical shift of this proton in both protonated and deprotonated forms.

At this stage of deprotonation the complex does not react with dichloromethane; it can be stored in solution under dry anaerobic conditions for at least 1 week and characterized spectroscopically. An important feature of the spectrum recorded after disappearance of the NH signal is a group of peaks derived from protons of one phenyl that are shifted about 1.5 ppm upfield (Figure 8D) with respect to their positions in **2**. Such a substantial and selective shift can be accounted for by the close vicinity of a molecule that possesses an aromatic current being in contact with only one phenyl out of the four. We assume that there is a specific intermolecular interaction leading to formation of a symmetric dimer. Mass spectrometry supports formation of the bis(porphyrinoid) system. The electrospray ionization mass spectrum of negative ions reveals the presence of deprotonated monomeric complex $[\mathbf{2}]^-$ (m/z = 669, 100%) and dimeric species $[(\mathbf{2})_2\mathrm{K}]^-$ (m/z = 1377, 30%). It suggests that the potassium cation may act here as a bridge between deprotonated nitrogens of two inverted pyrrole units. Formation of dimeric species in which external nitrogen

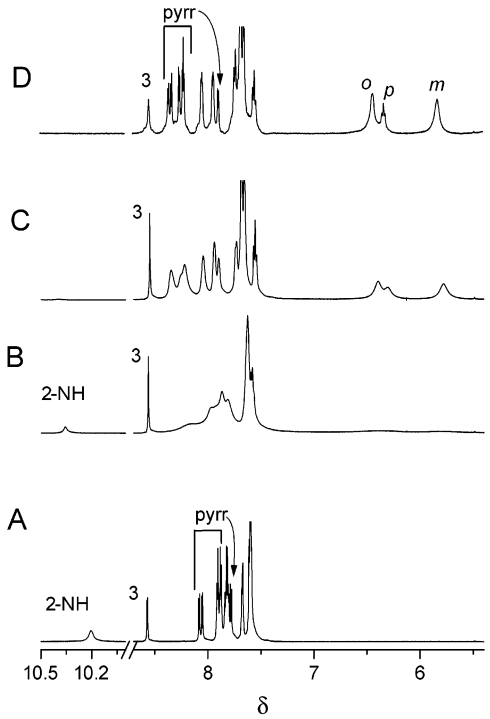


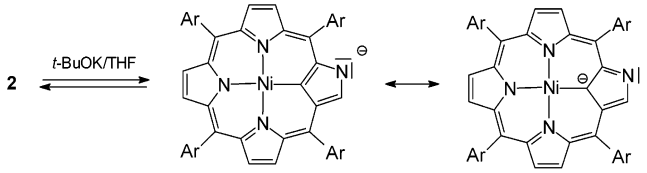
FIGURE 8. Selected ^{1}H NMR spectra recorded in the course of titration of **2** ($CDCl_2$ solution) with *t*-BuOK (THF solution): A, 0 equiv; B, 0.2 equiv; C, 0.9 equiv; D, 1.5 equiv of the base. $T = 298$ K.

is involved in coordination to the metal ion has been reported recently for the zinc complexes of the inverted porphyrin.[5h] Alternatively, formation of a symmetric hydrogen bond involving nitrogen atoms of one molecule of **2** (H-donor) and one of [**2**]$^-$ (H-acceptor) can be proposed. Lack of the bridging proton signal in the NMR spectrum may be due to its broadening by fast chemical exchange and the strong interaction with two quadrupolar nuclei of nitrogen.

The further increase of *t*-BuOK concentration causes broadening of all lines in ^{1}H NMR spectrum, low-field shift, and eventually disappearance of the high-field-shifted phenyl signals. A slow reaction with dichloromethane simultaneously starts, resulting in asymmetric dimer **8** with a 2,21-CD_2-linker. These observations suggest that proton abstraction from **2** proceeds through two consecutive stages, giving an intermediate product that is less reactive toward alkylation.

Proton abstraction from the external nitrogen is expected to promote formation of 2-substituted inverted porphyrins rather than their 21-substituted isomers. To prove this hypothesis, one should show exclusive or dominating formation of N-substituted monomers or *N*,*N*′-alkylene-linked dimers in each case when base is strong enough to effectively deprotonate external nitrogen. Although such a situation takes place in the case of reaction with ethylene bromide, it does not for propylene bromide. Dihalomethanes can substitute proton on the external nitrogen, but formation of a symmetrical *N*,*N*′-methylene-linked bis(carbaporphyrinoid) is always a disadvantageous process in comparison with formation of C,N′-linked species. The fact that under basic conditions **2** is activated toward the reaction on the inner carbon can be accounted for by assuming a shift of the

SCHEME 6. Proposed mesomeric forms of [2]$^-$



[**2**]$^-$

electron density from the anionic nitrogen onto the coordinated carbon (Scheme 6). The just described interaction between two molecules of the starting complex that presumably involves external nitrogen may be, in some cases, responsible for the higher reactivity of internal carbon 21-C in comparison with 2-N.

Protonation of the Internal Carbon. Protonation of the unsubstituted starting complex **2** and nickel(II) or copper(II) complexes methylated on the external nitrogen takes place on the internal carbon 21-C.[4e,5,6] Although addition of proton to the coordination core changes the overall charge of the complex, there is no ligation of an anion to the nickel(II) upon protonation. Consequently, the system remains diamagnetic.

Methylene groups of the substituents bound to the external nitrogen in **7** or **12** can be exploited as a diastereotopic probe if the protonation/deprotonation process is slow enough on the NMR time scale to lift the effective symmetry plane in these prochiral species.

For the complex **7** that contains an alkoxymethyl substituent on the external nitrogen, we have carried out a ^{1}H NMR-controlled titration with trifluoroacetic acid (TFAH) at low temperature (213 K, $CDCl_3$) in order to slow chemical exchange between the protonated and unprotonated species. On the basis of the ^{1}H−^{13}C HMQC (Figure 9) and HMBC experiments, the high-field signal (−2.59 ppm) appearing upon addition of TFAH is assigned to the proton on the 21-C that changes its hybridization from sp^2 to sp^3. This can be deduced on the basis of its chemical shift in ^{13}C NMR (35.9 ppm). The pyramidal environment of the internal carbon implies the chirality of the molecule induced by protonation. Indeed, signals of the methylene protons of the 2-alkoxymethyl group are no longer degenerate as in **7** (Figure 2D). In the case of [**7**−H]TFA, 1′-CH_2 appears as an AB system (5.87, 5.29 ppm, $^2J_{AB} = 8.3$ Hz), while the methylene of the ethoxyl fragment (3′-CH_2) gives two ill-resolved multiplets (2.32, 2.42 ppm). The system remains aromatic or even enhances its ring current effects in comparison to the unprotonated species. This can be concluded on the basis of the bigger downfield shift of pyrrole protons, which appear in the spectrum of [**7**−H]TFA in the region of 8.2−8.7 ppm (7.7−8.1 ppm for **7**), with proton 3 being at 9.3 ppm (8.6 for **7**). Also the high-field position of the 21-CH signal is due to the aromatic character of the protonated complex. It implies the quaternary character of the external nitrogen (Scheme 7).

Analogous results can be obtained for **12** (Scheme 7). In this case, addition of a 5-fold excess of TFAH to the CD_2Cl_2 solution causes appearance of 21-CH resonance at −2.61 ppm (233 K). Instead of two triplets (3.425 and 4.082 ppm, $J = 6.2$ Hz) of bromoethyl substituent in the spectrum of **12**, there are four ill-resolved multiplets

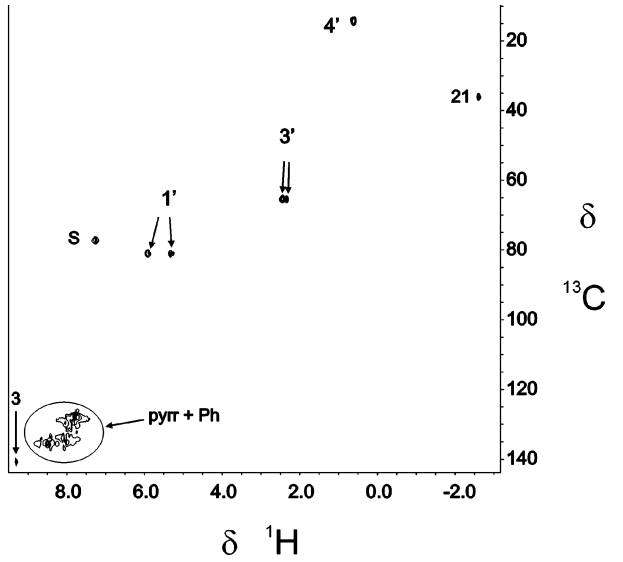
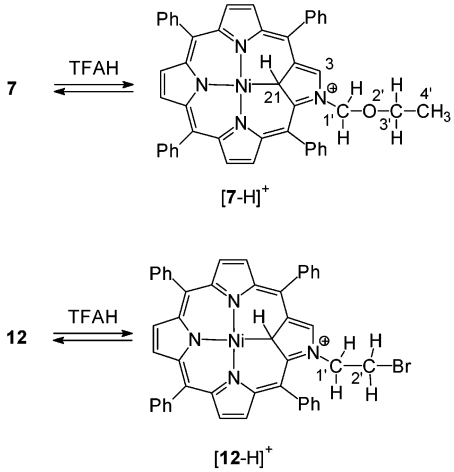


FIGURE 9. ^{1}H−^{13}C HMQC spectrum of [**7**−H]TFA ($CDCl_3$, 213 K). Assignments: pyrr, *β*-pyrrole; Ph, *meso*-phenyls, s, $CHCl_3$; the other labels follow those of Scheme 7.

SCHEME 7. Protonation of the externally alkylated complexes 7 and 12



(2.86, 3.13 and 4.72, 4.77 ppm) of diastereotopically differentiated methylene protons observed for [**12**−H]-TFA.

Weaker acids, like 2-bromopropionic acid, apparently do not produce proton concentration sufficient to protonate **7**, since its ^{1}H NMR spectrum in $CDCl_3$ at 213 K remains unchanged, even after addition of a 10-fold molar excess of the acid. On the other hand, addition of hydrochloric acid in the form of $CDCl_3$ saturated with a dry gaseous HCl does not allow observation of the well-defined NMR spectrum of the protonated complex. It seems that even at low temperature (203 K in CD_2Cl_2) the chemical exchange is fast in this case. This can be a consequence of a lack of stabilizing interaction between positively charged macrocyclic ligand and chloride anion that may occur in the case of carboxylic acid. Such a specific interaction between anions and 21-C-protonated nickel(II) complexes has been observed in the case of inverted *β*-heptaalkylporphyrins.[6]

Conclusions

We have shown that the reactivity of inverted pyrrole in the organometallic nickel(II) complex of inverted porphyrin toward dihalogenalkanes can lead to a variety of products, relative yields of which can be controlled by the reaction conditions. The reaction takes place either on the 21-C, i.e., within the coordination sphere of nickel(II) ion, or on the macrocycle perimeter. Strong nucleophiles like ethoxide ion preclude formation of bis(carbaporphyrinoids) that can be obtained in the reaction of **2** with dihalomethanes.[8] An analogous basic system does not prevent formation of dimer in the reaction of dibromoethane.

The presence of nickel(II) ion coordinated to the inverted pyrrole is crucial for the alkylation of the inverted pyrrole, but clearly it facilitates alkylation of the external nitrogen under basic condition. In fact, we observe no alkylation of the inverted porphyrin free base **1** with any of the dihalogenalkanes that have been effectively used in the reaction with **2**. Similarly, there is no reaction of dihalomethanes with the silver(III) complex **5**, despite the well-exposed position and potentially nucleophilic character of the outer nitrogen. It seems that the reactivity of the inverted pyrrole is related to the excess of the negative charge generated by deprotonation of the external nitrogen.

The most promising products of alkylation are those in which internal alkylation leaves the external nitrogen unoccupied and thus susceptible to protonation,[7] coordination, or hydrogen bonding. Studies on these subjects are underway.

Experimental Section

General. Mass spectra were recorded using the electrospray and electron impact mass spectrometry techniques.

Preparation of Precursors. 5,10,15,20-Tetraphenyl-2-aza-21-carbaporphyrin (**1**), 5,10,15,20-tetratolyl-2-aza-21-carbaporphyrin (**1a**), 5,10,15,20-tetraphenyl-2-aza-21-carbaporphyrinatonickel(II) (**2**), and 5,10,15,20-tetratolyl-2-aza-21-carbaporphyrinatonickel(II) (**2a**) were synthesized according to known procedures.[1,3]

Synthesis of 5,10,15,20-Tetraphenyl-21-ethoxymethyl-2-aza-21-carbaporphyrinatonickel(II) (6). 5,10,15,20-Tetraphenyl-2-aza-21-carbaporphyrinatonickel(II) (**2**) (30 mg, 0.045 mmol) was dissolved in 50 mL of deareated dichloromethane. After addition of 200 *μ*L of sodium ethoxide solution in ethanol (0.7 M), the mixture was refluxed for 4 h under the nitrogen. The solvent was then evaporated under reduced pressure and the solid residue was dissolved in dichloromethane and chromatographed on a silica gel column. The first greenish band that eluted with dichloromethane consists of small amount of starting complex **2** and 5,10,15,20-tetraphenyl-2-ethoxymethyl-2-aza-21-carbaporphyrinatonickel(II) **7**. The second brown-reddish band that contained **6** was eluted with a dichloromethane/chloroform mixture (1:1 v/v) and crystallized from CH_2Cl_2/hexane. Yield: 20 mg (60%). ^{1}H NMR (500 MHz, 298 K, $CDCl_3$): δ = 9.87 (1H, s), 8.72 (1H, d, J_{AB} = 5.0 Hz), 8.71 (1H, d, J_{AB} = 5.0 Hz), 8.50 (2H, overlapping doublets J_{AB} = 5.0 Hz), 8.45 (1H, d, J_{AB} = 4.5 Hz), 8.42 (1H, d, J_{AB} = 4.4 Hz), 8.26 (2H, b), 8.09 (2H, b), 8.05 (1H, b), 7.98 (1H, b) 7.85−7.65 (12H, overlapping multiplets), 1.88 (1H, m), 1.84 (1H, m), 0.37 (3H, t, ^{3}J = 6.9 Hz), −1.29 (1H, d, ^{2}J = 9.6 Hz), −1.39 (1H, d, ^{2}J = 9.6 Hz). ^{13}C NMR (125 MHz, 298 K, $CDCl_3$): δ = 179.5, 156.2, 156.0, 153.6, 152.9, 145.0, 149.2, 147.5, 146.7, 141.1, 145.0, 140.6, 140.3, 136.0, 135.8, 134.7, 134.2, 134.0, 133.8, 133.5, 132.8, 132.8, 132.3, 131.8, 131.7647, 128.8, 128.1, 128.0,

128.0, 127.8, 127.5, 126.9, 126.4, 124.5, 122.9, 74.9, 69.5, 64.6, 36.5, 14.5. UV/vis (CH_2Cl_2): λ_{max} (log ϵ) = 341 (4.20), 429 (4.60), 460 (sh), 595 (sh), 715 (sh), 793 (sh) nm. HRMS (EI): m/z = 729.2138 (729.2159 for $C_{47}H_{34}N_4ONi + H^+$).

Synthesis of 2-Ethoxymethyl-5,10,15,20-tetraphenyl-2-aza-21-carbaporphyrinatonickel(II) (7). A mixture of **2** (10 mg, 0.015 mmol) in deaerated dichloromethane/ethanol (20 and 5 mL, respectively), dibromomethane (0.5 g, 2.9 mmol), 1 mg of dibenzo[18]-crown-6, and a suspension of 5 mg of potassium carbonate was refluxed for 4 h under the nitrogen. The solvent was evaporated; the residue was dissolved in dichloromethane and chromatographed on a silica gel column with dichloromethane as an eluent. The fastest moving brownish-green band contained **7**. The product was crystallized from a dichloromethane/hexane mixture. Yield: 4 mg (37%). ^{1}H NMR (500 MHz, 298 K, $CDCl_3$): δ = 8.52 (1H, s), 8.01(1H, d, J_{AB} = 5.2 Hz), 7.91 (1H, d, J_{AB} = 5.2 Hz), 7.87 (1H, d, J_{AB} = 5.0 Hz), 7.86−7.77 (8H, overlapping multiplets), 7.56 (1H, d, J_{AB} = 5.2 Hz), 7.73 (1H, d, J_{AB} = 4.9 Hz), 7.63−7.50 (13H, overlapping multiplets), 5.00 (2H, s,), 3.19 (2H, q, J = 7.0 Hz), 0.99 (3H, t, J = 7.0 Hz). ^{13}C NMR (125 MHz, 298 K, $CDCl_3$, partial data): δ = 154.1, 151.7, 150.2, 149.5, 149.1, 146.3, 145.1, 144.7, 141.1, 139.4, 134.5, 133.4, 132.8, 132.6, 132.3, 130.4, 130.2, 128.3, 127.7, 127.4, 126.9, 125.8, 124.2, 123.4, 123.3,122.3, 79.8, 64,7, 14.8. UV/vis (CH_2Cl_2): λ_{max} (log ϵ) = 361 (4.60), 427 (4.86), 460 (4.60), 522 (sh), 560 (3.92), 593 (sh), 649 (sh), 720 (3.64), 789 (3.64), MS (ESI): m/z = 729.2 (729.2 for $C_{47}H_{34}N_4ONi + H^+$).

Reaction of 5,10,15,20-tetraphenyl-2-aza-21-carbaporphyrin (2) with dichloromethane was carried out in the inert atmosphere of a glovebox. To a solution of **2** (20 mg, 0.03 mmol) in dichloromethane (20 mL) was added potassium *tert*-butoxide (0.1 mL of 1 M solution in THF), and the mixture was stirred for 3 days. The solvents were then evaporated. The molar ratios of the substrate **2** and dimeric products **8** and **9** in the crude mixture (1:0.5:0.03) were estimated by ^{1}H NMR spectrum recorded for a $CDCl_3$ extract of the solid residue. The optimized synthesis of **8** as well as spectroscopic characterization of **8** and **9** were reported previously.[8]

Synthesis of Ethylenebis(21,21′-(5,10,15,20-tetraphenyl-2-aza-21-carbaporphyrinatonickel (II))) (11). A mixture of **2** (30 mg, 0.045 mmol) and 1,2-dibromoethane (400 mg, 2.12 mmol) in dichloromethane/ethanol (20/2 mL) containing a suspension of potassium carbonate (5 mg) was stirred for 5 days in darkness under a blanket of nitrogen. After that period, solvents were evaporated, and the solid residue was dissolved in dichloromethane and chromatographed on a silica gel column. The first greenish band eluted with dichloromethane contained unreacted **2**, while the second brownish band consisted of **12**. The third brownish band eluted with a dichloromethane/chloroform mixture (50/50 v/v) and contained **11** that was crystallized from a dichloromethane/hexane mixture. Yield: 16 mg (52%). ^{1}H NMR (500 MHz, 298 K, $CDCl_3$): δ = 8.493 (1H, d, J = 5.0 Hz), 8.487 (1H, d, J = 4.5 Hz), 8.482 (2H, d, J = 5.0 Hz), 8.470 (1H, d, J = 4.6 Hz), 8.456 (1H, s, 3), 8.451 (1H, d, J = 4.6 Hz), 8.437 (1H, d, J = 5.2 Hz), 8.436 (2H, b), 8.431 (1H, s), 8.425 (1H, d, J = 5.2 Hz), 8.382 (2H, d, J = 6.4 Hz), 8.339 (1H, d, J = 4.8 Hz), 8.313 (1H, d, J = 4.8 Hz), 8.229 (1H, d, J = 4.8 Hz), 8.201 (1H, d, J = 4.8 Hz), 8.064 (1H, d, J = 7.1 Hz), 8.020 (1H, d, J = 7.1 Hz), 7.980 (1H, d, J = 7.3 Hz), 7.937 (1H, d, J = 7.3 Hz), 7.921 (1H, d, J = 7.6 Hz), 7.905 (1H, d, J = 8.2 Hz), 7.888 (1H, d, J = 8.2 Hz), 7.872 (1H, d, J = 7.1 Hz), 7.85−7.62 (8H, overlapping multiplets), 7.57−4.2 (4H, b), 7.396 (2H, m), 7.294 (2H, m), 7.17 (8H, b), 6.04 (4H, b), −4.61 to −5.02 (4H, overlapping multiplets. UV/vis(CH_2Cl_2): λ_{max} (log ϵ) = 362 (4.60), 421 (4.70), 466 (sh), 559 (sh), MS (ESI): m/z = 1369.5 (1369.9 for $C_{90}H_{58}N_8Ni_2$), 685.2 ([M + 2H]$^{2+}$). Anal. Found: %C, 76.65; %H, 4.10; %N, 7.68. Calcd for $C_{90}H_{58}N_8Ni_2 \cdot H_2O$: %C, 77.03; %H, 4.42; %N, 7.99.

Ethylenebis(21,21′-(5,10,15,20-tetrakis(p-tolyl)-2-aza-21-carbaporphyrinatonickel(II))) (11a) was obtained in the same way as **11** using 5,10,15,20-tetrakis(*p*-tolyl)-2-aza-21-carbaporphyrinatonickel(II) **2a** instead of **2** as a starting material. ^{1}H NMR (500 MHz, 298 K, $CDCl_3$): δ = 8.505 (1H, d, J = 4.6 Hz), 8.498 (1H, d, J = 4.6 Hz), 8.473 (1H, d, J = 4.6 Hz), 8.464 (1H, d, J = 4.6 Hz), 8.415 (1H, d, J = 5.0 Hz), 8.409 (1H, d, J = 5.0 Hz), 8.397 (1H, s), 8.385 (1H, s), 8.384 (1H, d, J = 5.0 Hz), 8.374 (1H, d, J = 4.6 Hz), 8.362 (1H, b), 8.337 (1H, d, J = 5.0 Hz), 8.328 (1H, b), 8.307 (1H, d, J = 5.0 Hz), 8.294 (1H, b), 8.280 (1H, b), 8.254 (1H, d, J = 5.0 Hz), 8.221 (1H, d, J = 5.0 Hz), 7.936 (2H, d, J = 7.3 Hz), 7.912 (2H, d, J = 8.2 Hz), 7.843 (2H, d, J = 7.3 Hz), 7.825 (2H, d, J = 7.8 Hzl), 7.721 (2H, d, J = 7.8 Hz), 7.691 (2H, d, J = 7.3 Hz), 7.55−7.45 (4H, overlapping multiplets), 6.970 (8H, b), 6.309 (4H, b), 2.729 (3H, s), 2.722 (3H, s), 2.717 (3H, s), 2.711 (3H, s), 2.397 (6H, s), 2.354 (6H, s), −4.65 to −4.95 (4H, overlapping multiplets), ^{1}H NMR (500 MHz, 233 K, $CDCl_3$): δ = 8.525 (1H, d, J = 5.0 Hz,), 8.511 (1H, d, J = 5.0 Hz), 8.493 (1H, d, J = 4.5 Hz), 8.479 (1H, d, J = 4.5 Hz), 8.421 (1H, d, J = 4.6 Hz), 8.396 (1H, d, J = 4.6 Hz), 8.379 (1H, s), 8.351 (1H, s), 8.340 (2H, overlapping multiplets), 8.320 (1H, m), 8.300 (1H, d, J = 4.6 Hz), 8.290 (1H, d, J = 5.0 Hz), 8.257 (1H, d, J = 4.6 Hz), 8.200 (1H, d, J = 4.6 Hz), 7.964 (2H, m), 7.946 (2H, m), 7.852 (2H, m), 7.837 (2H, m), 7.758 (2H, m), 7.713 (2H, m), 7.551 (2H, m), 7.513 (2H, overlapping multiplets), 7.435 (1H, m), 7.390 (1H, m), 7.22−7.13 (4H, overlapping multiplets), 6.805 (1H, m), 6.757 (2H, m), 6.711 (1H, m), 5.822 (1H, m), 5.787 (1H, m), 5.706 (1H, m), 5.651 (1H, m), 2.731 (3H, s), 2.722 (3H, s), 2.717 (3H, s), 2.710 (3H, s), 2.372 (3H, s), 2.365 (3H, s), 2.344 (3H, s), 2.334 (3H, s), −4.8 to −5.1 (4H, overlapping multiplets). ^{13}C NMR (125 MHz, 233 K, $CDCl_3$): δ = 177.3, 176.7, 153.9, 153.7, 152.0, 151.9, 151.8, 151.6, 148.0, 147.3, 138.3, 138.2, 137.6, 137.4, 137.3, 136.9, 135.6, 135.6, 135.3, 135.2, 135.1, 135.0, 134.9, 134.9, 134.7, 134.5, 134.3, 134.2, 133.4, 132.8, 132.0, 131.8, 131.7, 131.4, 128.5, 128.3, 128.2, 127.9, 127.8, 127.8, 127.8, 127.8, 126.5, 126.4, 125.7, 124.8, 124.5, 123.9, 123.1, 36.9, 32.3, 21.9, 21.8, 21.7, 21.6, 21.5, 21.3, 21.0. MS (ESI): m/z = 1480.6 (1481.1 for $C_{98}H_{74}N_8Ni_2$), 740.6 ([M + 2H]$^{2+}$). Anal. Found: %C, 77.50; %H, 5.00; %N, 7.60. Calcd for $C_{98}H_{74}N_8Ni_2 \cdot H_2O$: %C, 77.67; %H, 5.15; %N, 7.39.

2-(2′-Bromoethyl)-5,10,15,20-tetraphenyl-2-aza-21-carbaporphyrinatonickel(II) (12). A mixture of **2** (30 mg, 0.045 mmol) and 1,2-dibromoethane (400 mg, 2.12 mmol) in THF (30 mL) containing 0.45 mmol of potassium *tert*-butoxide was refluxed in darkness for 2 days in the inert atmosphere of a glovebox. After that period, the solvent was evaporated and the solid residue was dissolved in dichloromethane and chromatographed on a silica gel column. The first greenish band eluted with dichloromethane contained unreacted **2**, while the second brownish band consists of **12** that was crystallized from dichloromethane/hexane mixture. Yield: 24 mg (68%). ^{1}H NMR (500 MHz, 298 K, $CDCl_3$): δ = 8.408 (1H, s), 8.009 (1H, d, J = 4.9 Hz), 7.903 (1H, d, J = 4.9 Hz), 7.871 (1H, d, J = 4.9 Hz), 7.789 (1H, d, J = 4.9 Hz), 7.86−7.83 (2H, overlapping multiplets), 7.82−7.89 (6H, overlapping multiplets), 7.756 (1H, d, J = 4.9 Hz), 7.723 (1H, d, J = 4.9 Hz), 7.65−7.50 (12H, overlapping multiplets), 4.113 (2H, d, J = 6.7 Hz), 3.378 (2H, d, J = 6.7 Hz). ^{13}C NMR (125 MHz, 298 K, $CDCl_3$): δ = 153.6, 151.5, 151.4, 149.5, 148.1, 145.9, 144.5, 141.2, 139.7, 138.9, 133.5, 133.2, 133.1, 133.1, 132.8, 132.7, 132.3, 132.1, 131.5, 131.0, 130.2, 128.6, 128.4, 127.8, 127.7, 127.6, 127.2, 127.1, 127.0, 126.8, 125.6, 122.8, 122.4, 118.2, 117.2, 53.4, 52.6, 30.9. UV/vis (CH_2Cl_2): λ_{max} (log ϵ) = 242 (sh), 363 (4.61), 428 (4.87), 462 (4.63), 526 (sh), 559 (3.94), 594 (sh), 654 (sh), 720 (3.63), 790 (3.64), MS (ESI): m/z = 777.5 (778.3 for $C_{46}H_{31}N_4BrNi$).

Crystals suitable for X-ray analysis were obtained by slow diffusion of hexane to the solution of 12 in chloroform. Crystal data are given in Table S1 of the Supporting Information, together with refinement details. All measurements were performed at low temperature using an Oxford Cryosystem device on a Kuma KM4CCD κ-axis diffractometer with graphite-monochromated MoKα radiation. The crystal was positioned at 65 mm from the CCD camera. 612 frames were measured

at 0.75° intervals with a counting time of 9 s. Accurate cell parameters were determined and refined by least-squares fit of 3200 strongest reflections. The data were corrected for Lorentz and polarization effects. Analytical absorption correction and data reduction and analysis were made using the CrysAlis suit of programs.[18] The structure was solved by the heavy atom method (SHELX97[19]) and refined by the full-matrix least-squares method on all F^2 data using the SHELXL97[20] program. Non-hydrogen atoms were refined with anisotropic displacement parameters; hydrogen atoms were included from geometry of molecules and $\Delta\rho$ maps but were not refined. Results of refinement suggest disorder phenomena in the region of inverted pyrrole. They are reflected by occupancy parameters equal to 0.7 for Br(1) as well as for C(46) and C(47) atoms. Simultaneously, the final $\Delta\rho$ map shows two additional maxima (about 3.5 e•Å^{-3}) in the same region of the molecule, suggesting an alternative orientation of the whole molecule in the crystal. Formally it involves a permutation of external nitrogen and adjacent carbon. We believe that disorder of this alternative alkyl chain is responsible for those two maxima that show two other positions of Br atoms.

Synthesis of 5,10,15,20-Tetraphenyl-21-allyl-2-aza-21-carbaporphyrinatonickel(II) (14). A mixture of **2** (30 mg, 0.045 mmol), 1,3-dibromopropane (100 mg, 0.5 mmol), and potassium *tert*-butoxide (0.2 mmol) in THF solution (30 mL) was stirred for 3 days at room temperature in the inert atmosphere of a glovebox. After that period, solvent was evaporated under reduced pressure. The solid was dissolved in dichloromethane and chromatographed on a silica gel column. The second brown-reddish band that contained **14** was eluted with dichloromethane and crystallized from a CH_2Cl_2/hexane mixture. Yield: 23 mg (71%). ^{1}H NMR (500 MHz, 298 K, $CDCl_3$): δ = 9.82 (1H, s), 8.66 (1H, d, J_{AB} = 4.8 Hz), 8.64 (1H, d, J_{AB} = 5.0 Hz), 8.49 (2H, overlapping doublets J = 4.8 Hz), 8.45 (1H, d, J_{AB} = 4.8 Hz), 8.41 (1H, d, J_{AB} = 4.8 Hz), 8.22 (2H, b), 8.06 (2H, b), 8.02 (1H, b), 7.97 (1H, b) 7.8−7.6 (12H, overlapping multiplets), 4.14 (1H, d, J = 9.9 Hz), 3.75 (1H, m), 3.38 (1H, d, J = 17.0 Hz), −2.31 (1H, dd, ^2J = 12.7 Hz, ^3J = 7.0 Hz), −2.35 (1H, dd, ^2J = 12.6 Hz, ^3J = 6.9 Hz). ^{13}C NMR (125 MHz, 213 K, $CDCl_3$): δ = 178.6, 156.2, 155.7, 153.6, 152.5, 150.1, 149.4, 147.4, 146.7, 140.6, 140.5, 139.9, 139.7, 136.3, 136.1, 135.5, 134.8, 134.6, 134.4, 134.3, 134.0, 133.9, 133.8, 132.9, 132.6, 132.5, 132.0, 131.8, 128.2, 128.1, 128.0, 127.9, 127.7, 127.5, 126.9, 125.0, 123.4, 114.4, 53.7, 36.1, 35.4. UV/vis (CH_2Cl_2): λ_{max} (log ϵ) = 354 (4.29), 432 (4.59), 462 (sh), 610 (sh), 751 (2.30) nm. HRMS (EI): m/z = 711.1853 (711.2059 for $C_{47}H_{33}N_4Ni + H^+$).

Preparation of Samples. Dichloromethane-d_2 and chloroform-*d* used for NMR samples were passed through basic alumina before use. The solution of the trifluroacetic acid in $CDCl_3$ or in CD_2Cl_2 was added by syringe to the NMR tube containing **7** or **12** as a neutral form. The progress of the reaction was followed by ^{1}H NMR spectroscopy. The samples of **2** for NMR or spectrophotometric titration with potassium *tert*-butoxide were prepared in the inert atmosphere of a glovebox. A solution of *t*-BuOK in THF was added by syringe to the NMR tube or quartz spectrophotometric cell containing a solution of **2** in dichloromethane and sealed with silicon septa.

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Supporting Information Available: Tables of crystal data, bond lengths and angles, molecular models of **11**, X-ray crystallographic file (CIF), and additional optical and NMR spectra. This material is available free of charge via the Internet at http://pubs.acs.org.

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