Copper(II) Complexes of Inverted Porphyrin and Its Methylated Derivatives

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The inverted porphyrins 2-aza-5,10,15,20-tetraphenyl-21-carbaporphyrin (CTPPH$_2$) and its methylated derivatives 2-aza-2-methyl-5,10,15,20-tetraphenyl-21-carbaporphyrin (2-NCH$_3$CTPPH) and 2-aza-2-methyl-5,10,15,20-tetraphenyl-21-methyl-21-carbaporphyrin (2-NCH$_3$-21-CH$_3$CTPPH) stabilize the rare organocopper(II) complexes (CTPP)Cu^{II} (**1**), (2-NCH$_3$CTPP)Cu^{II} (**2**), (CTPPH)Cu^{II}X (**3-X**), (2-NCH$_3$CTPPH)Cu^{II}X (**4-X**) (X = Cl$^-$, TFA), and (2-NCH$_3$-21-CH$_3$CTPP)Cu^{II}Cl (**5**). The EPR spectra recorded for **1**, **2**, **4**, and **5** revealed typical features diagnostic of the copper(II) electronic structure. The superhyperfine coupling pattern indicates a presence of three nitrogen donors in the first coordination sphere. An addition of HX acid to **1** and **2** to yield the species **3-X** and **4-X**. The reaction mechanism includes protonation of the inner C(21) carbon accompanied by an axial coordination of anion. Methylation of (2-NCH$_3$CTPP)Cu^{II} (**2**) with methyl iodide resulted in formation of (2-NCH$_3$-21-CH$_3$CTPP)Cu^{II}Cl (**5**) which implies an existence of a σ-carbanion−copper(II) bond in **2**. The ^{2}H NMR investigations carried out for the pyrrole deuterated derivatives (CTPP-d_7)Cu^{II}, (2-NCH$_3$-21-CH$_3$CTPP-d_7)Cu^{II}-Cl, and the methyl deuterated (2-NCH$_3$-21-CD$_3$CTPP)Cu^{II}Cl one confirmed independently the copper(II) electronic structure with the considerable d$_{x^2-y^2}$ metal orbital contribution to the SOMO. The redox properties of copper(II) inverted porphyrins were studied by the cyclic and differential pulse voltammetry. The halfwave potentials indicate a metal-centered oxidation of **1** (390 mV) and **2** (343 mV). The dimethylated homologue **5** reveals the reduction process at −224 mV attributed to the Cu^{II}/Cu^{I} transformation.

Introduction

2-Aza-21-carbaporphyrin (inverted porphyrin) remains the only porphyrin isomer that retains a molecular frame of a regular porphyrin.[1−6] The unique structural features of 2-aza-5,10,15,-20-tetraphenyl-21-carbaporphyrin (CTPPH$_2$)[1,2] and its peripherally methylated modification 2-methyl-2-aza-5,10,15,20-tetraphenyl-21-carbaporphyrin (2-NCH$_3$CTPPH)[4] as well as hexa- and heptaalkyl substituted derivatives 2-aza-3,7,8,12,13,17,18-hepataalkyl-21-carbaporphyrin (CHAPH$_2$)[3,6] result from a location of one of the pyrrolic C−H groups inside the macrocycle cavity due to a "confusion" of pyrrolic N and β-C atoms. The remarkable position of the β-carbon atom and an unusual labilization of the carbon(21)−hydrogen bond promoted nickel-(II) ion insertions which were accompanied by formation of a stable Ni^{II}−C(21) σ-bond.[1,4,6] Previously we have reported on characterization of (CTPP)Ni^{II} and (2-NCH$_3$CTPP)Ni^{II}.[1,4] In all nickel complexes studied to date the carbaporphyrin ligands exhibited a dianionic character. Thus the nickel(II) coordination requires a prearrangement step involving a protonation of the outer nitrogen.[1,4,7]

(CTPP)Ni^{II} and (2-NCH$_3$CTPP)Ni^{II} undergo reversible one-electron metal-centered oxidation to generate corresponding nickel(III) species.[8] Reactions of (CTPP)Ni^{II} or (2-NCH$_3$CTPP)-Ni^{II} with methyl iodide resulted in methylation of the "inner" C(21) carbon to produce (21-CH$_3$CTPP)Ni^{II} and (2-NCH$_3$-21-CH$_3$CTPP)Ni^{II}X complexes.[9]

The peculiar ability of inverted porphyrin or its methylated derivatives to stabilize unusual coordination modes, e.g., rare paramagnetic organonickel(II) species, should not be limited to nickel chemistry. Thus, a placement of a metal ion of interest in a suitably prearranged core of carbaporphyrin provides a promising route to create unprecedented metal−carbon bonds. For instance Furuta and co-workers have demonstrated that the inverted porphyrin acts as trianionic ligands stabilizing the silver(III) cation.[10]

In light of this observation we have turned our attention to organometallic chemistry of copper. In general the organometallic chemistry of copper is nearly exclusively focused on the metal oxidation state of +1.[11] Electron-rich organocopper(I) compounds are widely applied as useful reagents in numerous organic syntheses.[12] Organocopper(III) transient species were considered in the mechanism of a multiple bond activation via reactive π complexes. Their transformation into the σ-carbon copper(III) intermediate[13−16] was followed by reductive elimination. The role of trivalent organocopper in the reaction pathway

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Scheme 1
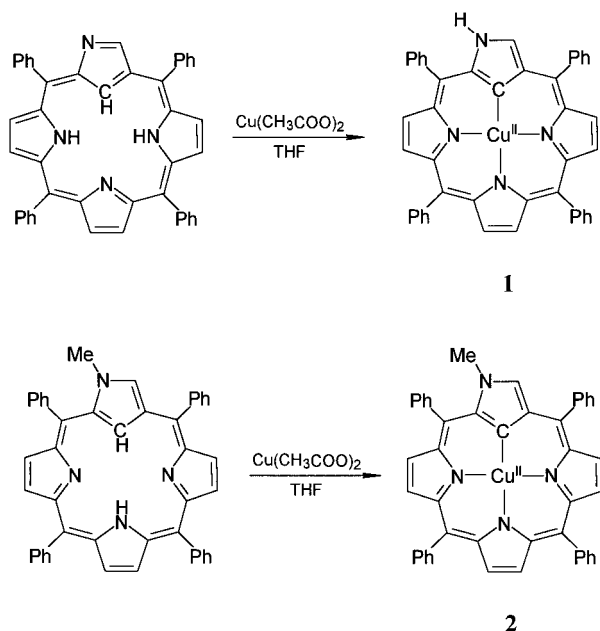
has been questioned on the basis of the electron density analysis.[17,18] Nonetheless the stable organometallic complexes of copper(III) were characterized by X-ray crystalography.[19−21]

In contrast to copper(I) and copper(III), no stable organo-copper(II) species have been reported to date. However, the transient σ-alkyl adducts of copper(II) have been postulated in the reactions of copper(I) complexes with aliphatic radicals obtained by pulse-radiolysis technique.[22−24]

Here we report on synthesis and spectroscopic characterization of copper(II) complexes of 2-aza-5,10,15,20-tetraphenyl-21-carbaporphyrin and its mono- and dimethylated derivatives. To the best of our knowledge these compounds represent the only examples of stable monomeric organometallic complexes of copper(II). The EPR spectroscopy is particularly informative with regard to the details of electronic structure of copper complexes.[25] Thus it has been applied to assign the electronic structure of all insertion products of copper(II) into carbapor-phyrin or its methylated derivatives.
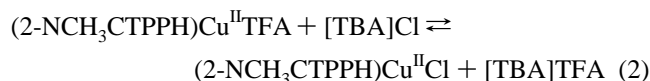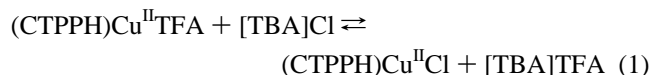
Results and Discussion

Synthesis and Characterization. Reaction of $Cu^{II}(CH_3COO)_2$ and $CTPPH_2$ or $2\text{-}NCH_3CTPPH$ under mild conditions (inert atmosphere, THF, 298 K, stirring for 5 h) resulted in formation of $(CTPP)Cu^{II}$ (**1**) or $(2\text{-}NCH_3CTPP)Cu^{II}$ (**2**), respectively (Scheme 1).

The EPR spectra recorded for **1** and **2** revealed several features which are typical for copper(II) complexes (Figure 1, trace A).[25−29] Significantly, the superhyperfine coupling pattern indicates a presence of three pyrrole nitrogen donors in the inner coordination sphere. The isotropic $^{63,65}Cu$ hyperfine constants are relatively small when compared to the copper(II) porphyrins and copper(II) monoheteroporphyrins although similar to those determined for copper(II) dioxaporphyrin.[25−29] The absolute values of the spin-Hamiltionian parameters determined for anisotropic spectra of frozen solutions do not differ from those obtained for typical copper(II) complexes.[25−29] This fact indicates that the orbital containing unpaired electron (SOMO) involves a predominant metal contribution. Consequently, the EPR spectra of **1** and **2** are essentially different from those expected for an alternative hypothetical ground electronic state with an unpaired electron localized mainly on the carbaporphyrin ligand. Such an electronic structure is feasible for a diamagnetic copper cation (Cu^I or Cu^{III}) coordinated by a carbaporphyrin radical.[30,31]

Formally, the inverted porphyrin ligand, as found for (CTPP)-Ni^{II}, is structurally related to one of $CTPPH_2$ tautomers,[7] i.e., 2-NHCTPPH which has been detected in the pyridine-d_5 solution.[32] This tautomer preserves the pyrrolic nature of the inverted ring. In this form only two inner protons 21-CH and 23-NH are available for the inner dissociation to create a dianion. $2\text{-}NCH_3CTPPH$ provides an analogous, conveniently preorga-nized structure for the similar coordination pattern. Similarities of the EPR as well as the optical spectral features of **1** and **2** strongly suggest the same coordination mode of inverted porphyrin and its 2-*N*-methylated homologue. In particular, a dianionic character of both macrocycles and presence of the hydrogen atom attached to the external nitrogen in $(CTPP)Cu^{II}$ can be inferred.

EPR titration of **1** and **2** with acids (TFA, HCl in dichlo-romethane) resulted in gradual spectroscopic changes that reflected a formation of new species: **3**-X and **4**-X respectively (Figure 1, traces B and C). The spin-Hamiltonian parameters of **3**-X and **4**-X, although similar for each acid used (HX), clearly depend on an anion introduced in the course of titration (Table 1). This fact indicates an axial coordination of an anionic ligand X. This conclusion has been also confirmed by a metathesis of **3**-TFA to **3**-Cl using an appropriate tetraalkylam-monium salt, e.g., [TBA]Cl.

$$(CTPPH)Cu^{II}TFA + [TBA]Cl \rightleftarrows$$
$$(CTPPH)Cu^{II}Cl + [TBA]TFA \quad (1)$$

$$(2\text{-}NCH_3CTPPH)Cu^{II}TFA + [TBA]Cl \rightleftarrows$$
$$(2\text{-}NCH_3CTPPH)Cu^{II}Cl + [TBA]TFA \quad (2)$$

Contrary to the reactivity of **3**-TFA and **4**-TFA, addition of [TBA]Cl to a dichloromethane solution of $(CTPP)Cu^{II}$ or $(2\text{-}NCH_3CTPP)Cu^{II}$ causes no EPR spectral changes. The reaction

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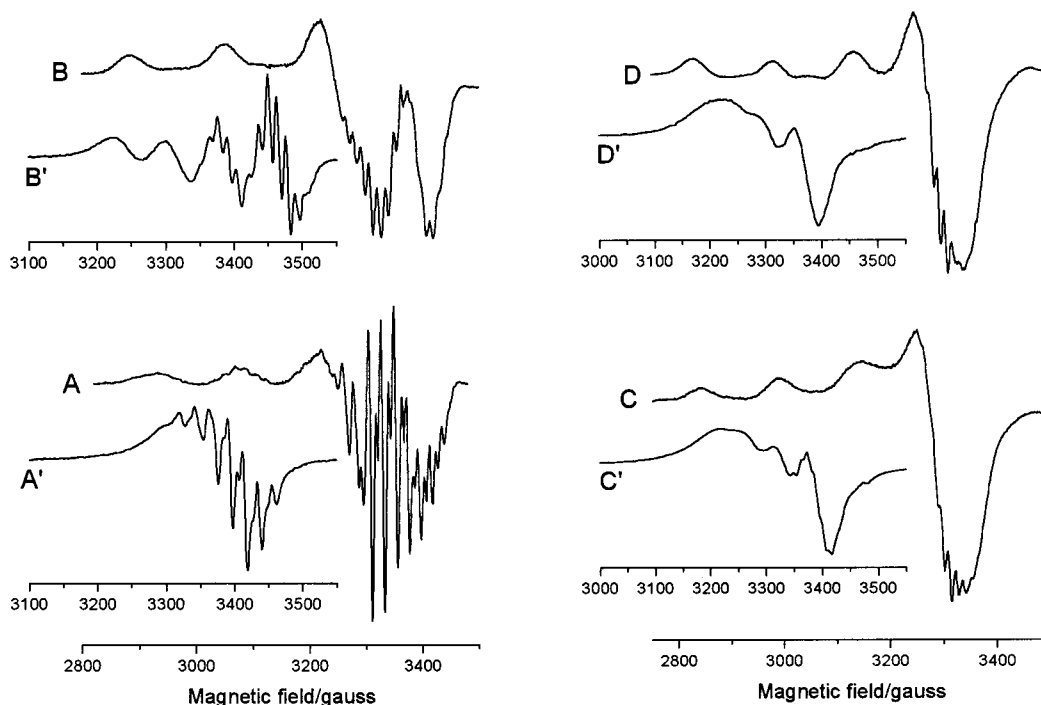(32) Furuta, H. Private communication, see ref 5, p 402.

Figure 1. EPR spectra (X-band, dichloromethane, 77 K): (A) (2-NCH$_3$CTPP)Cu^{II} (**2**); (B) (2-NCH$_3$CTPPH)Cu^{II}(TFA) (**4**-TFA); (C) (2-NCH$_3$-CTPPH)Cu^{II}Cl (**4**-Cl); (D) (2-NCH$_3$-21-CH$_3$CTPP)Cu^{II}Cl (**5**). Insets in each trace (A′, B′, C′, D′, respectively) present the corresponding isotropic spectra at 293 K. Conditions: microwave frequency ν = 9.4175 GHz for anisotropic spectra and 9.788 GHz for the isotropic spectra; microwave power 10 mW, modulation amplitude, 0.6 mT; modulation frequency 100 kHz.
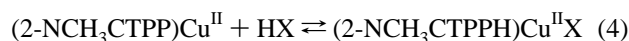
Table 1. Spin-Hamiltonian Parameters of Copper(II) Complexes of Inverted Porphyrins[a]

complex	$-A_{\parallel}{}^{Cu}$	$-A_{\perp}{}^{Cu}$	$g_{\parallel}$	$g_{\perp}$	$-A_o{}^{Cu}$	g_o	$A_o{}^N$
(CTPP)Cu (**1**)[b]	143	-37^d	2.139	2.057	23.0	2.070	18.3
(2-NCH$_3$CTPP)Cu (**2**)[b]	140	-27^d	2.142	(2.054, 2.026)^f	28.5	2.079	20.0
		$(-30.0, -19.2)^f$					
(CTPPH)Cu(TFA) (**3**-TFA)[c]	171	25^d	2.141	2.058	73.7	2.077	13.0
(CTPPH)CuCl (**3**-Cl)[c]	154	13^d	2.190	2.050	60.0	2.110	13.0
(2-NCH$_3$CTPPH)Cu(TFA) (**4**-TFA)[c]	167	18^d	2.142	2.071	67.5	2.074	13.0
(2-NCH$_3$CTPPH)CuCl (**4**-Cl)[c]	151	13^d	2.195	2.052	59.2	2.113	12.9
(2-NCH$_3$−21-CH$_3$CTPP)CuCl (**5**)[c]	155	12^d	2.202	2.055	59.6	2.094	13
(CTPP)^{63}Cu (**1**)[e]	129	-30^d	2.133	2.057	22.7	2.070	18.5

[a] Frozen solution spectra taken at 77 K, liquid solution spectra were recorded at 293 K. The solvent was toluene/dichloromethane mixture (80/20 v/v), unless indicated otherwise. Hyperfine constants are in 10^{-4} cm^{-1}. [b] Frozen solution ^{14}N hyperfine constants: in "parallel" region 18.0; in "perpendicular" region 12.2 and 20.8. [c] ^{14}N hyperfine constants in the perpendicular region is 13.0. [d] Calculated from the expression: $A_{\perp}{}^{Cu} = (3 A_o{}^{Cu} - A_{\parallel}{}^{Cu})/2$. [e] THF solution. [f] The best fit simulation results for orthorhombic symmetry.

of **1** and **2** with HX is reversible. The original EPR spectra of (CTPP)Cu^{II} or (2-NCH$_3$CTPP)Cu^{II} have been recovered after addition of a sterically hindered nitrogen base, 2,4,6-collidine, to the solution of **3**-X and **4**-X. The parallel titration has been followed by electronic spectra, showing the reversible acid−base dependence (Figure 2). Actually, the insertion reaction with Cu^{II}Cl$_2$ instead of Cu(CH$_3$COO)$_2$ as a copper source, into CTPPH$_2$ or 2-NCH$_3$CTPPH under mild conditions resulted in formation of species analogous to those produced in the course of titration of **1** or **2** with HCl, i.e., **3**-Cl and **4**-Cl.

The isotropic ^{14}N EPR hyperfine pattern for **3**-X and **4**-X can be reproduced by a simulation assuming that all three nitrogen atoms are practically magnetically equivalent, indicating a similar character of bonds formed between the copper(II) ion and each of the nitrogen donors. This structurally important observation excludes the possibility of protonation of any coordinated nitrogen atom and identifies a C(21) as the proton binding center. Altogether, the observed spectral changes accompany the reversible addition of acid to the copper(II) complexes according to equations:

$$(CTPP)Cu^{II} + HX \rightleftharpoons (CTPPH)Cu^{II}X \qquad (3)$$

$$(2\text{-}NCH_3CTPP)Cu^{II} + HX \rightleftharpoons (2\text{-}NCH_3CTPPH)Cu^{II}X \quad (4)$$

A similarity of EPR spectra recorded for (CTPPH)Cu^{II}X and (2-NCH$_3$CTPPH)Cu^{II}X (for given X) suggests that the coordination mode is similar for both inverted porphyrins. Thus, the reaction mechanism includes protonation of the inner C(21) carbon with a possible axial coordination of the accompanying anion (Scheme 2). This observation is consistent with small energy differences between the ligand tautomeric forms which can contribute in the coordination.[7,33]

At the present stage we can formally propose two alternative coordination modes of the 21-CH moiety in the protonated copper(II) complexes (Scheme 2). The first type involves a coordination of a pyramidal carbon in the η^1-fashion (**3a** and **4a**) and the copper(II) ion is four-coordinate. Here, the 21-carbaporphyrin core retains its dianionic nature accompanied

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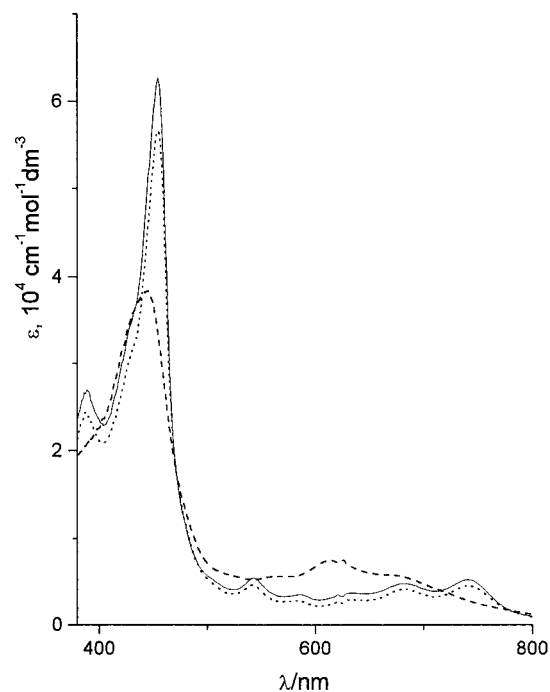
Figure 2. UV−vis absorption spectra (293 K, dichloromethane) of (2-NCH$_3$CTPP)Cu^{II} (**2**) (solid line); (2-NCH$_3$CTPPH)Cu^{II}TFA (**4**-TFA) (dashed line). The original UV spectrum of **2** has been recovered after addition of 2,4,6-collidine to the solution of **4**-TFA (dotted line).

however by the peripheral positive charge increase due to the protonation of the 2-N nitrogen. Alternatively one can consider a side-on η^1-fashion but the protonated carbon(21) preserves the trigonal geometry (**3b** and **4b**). In this case the copper(II) ion is five-coordinate and the protonated carbaporphyrin acts effectively as a ligand with a monoanionic coordination core. The positive charge in the system is compensated by a strong tendency to coordinate axially an anionic ligand.

Insertion of copper(II) into 2-aza-2,21-dimethyl-5,10,15,20-tetraphenyl-21-carbaporphyrin produced (2-NCH$_3$-21-CH$_3$-CTPP)Cu^{II}Cl (**5**). The EPR parameters of (2-NCH$_3$-21-CH$_3$-CTPP)Cu^{II}Cl resemble these of (CTPPH)Cu^{II}Cl and (2-NCH$_3$CTPPH)Cu^{II}Cl (Table 1). The spectroscopic pattern depends on the anionic ligand X, similarly as detected for (2-NCH$_3$CTPPH)Cu^{II}X or (CTPPH)Cu^{II}X. However no changes in isotropic spectra have been observed upon addition of the nitrogen base indicating lack of a labile proton in the molecule. Generally, as a results of steric constrains, the C(21) carbon atom, located inside the carbaporphyrin (methylated carbaporphyrin) crevice, is in position to participate in the bonding with copper(II) ion not only as a sp^2 σ-carbanion (**1** and **2**) but even in the C(21) protonated (**3** and **4**) or methylated (**5**) complexes. It may be anticipated that in the latter cases the bond is weaker.

The ^{2}H NMR spectroscopy has been used as an independent probe to determine the electronic structure of organocopper(II) complexes. Such an approach is complementary to the ESR studies of d^9 metalloporphyrins and heteroporphyrins[34−36] as it allows to observe directly the spin density delocalization on the macrocycle. On the basis of the ESR analysis, three representative species, i.e., (CTPP-d_7)Cu^{II}, (2-NCH$_3$-21-CH$_3$-CTPP-d_7)Cu^{II}Cl, and (2-NCH$_3$-21-CD$_3$CTPP)Cu^{II}Cl have been selected for ^{2}H NMR investigation (CTPP-d_7; 2-NCH$_3$-21-CH$_3$-CTPP-d_7−pyrrole protons are substituted with deuterons, 2-NCH$_3$-21-CD$_3$CTPP the deuterated methyl group is attached to the "inner" carbon). All pyrrole peaks of (CTPP-d_7)Cu^{II} are shifted downfield (Figure 3, trace A). They are widely spread over

Scheme 2
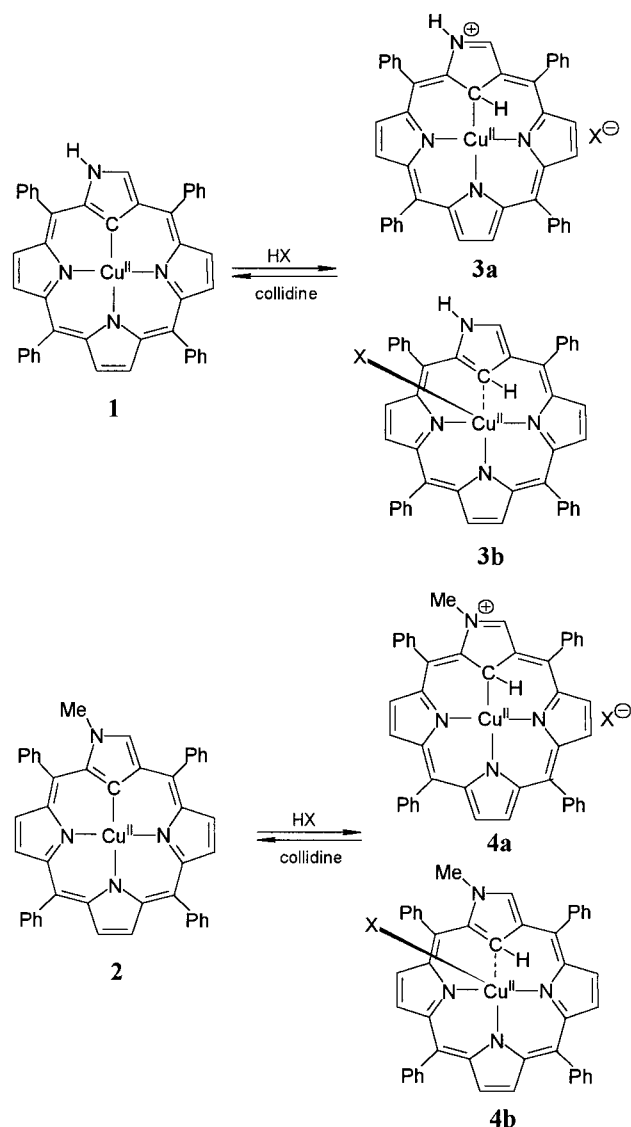
0−50 ppm. A similar NMR pattern has been determined for (2-NCH$_3$-21-CH$_3$CTPP-d_7)Cu^{II}Cl although here, in addition to the downfield set of pyrrole resonances, an upfield resonance has been detected (Figure 3, trace C). The downfield positions of the pyrrole resonances is consistent with the considerable d$_{x^2-y^2}$ metal orbital contribution to the SOMO and the σ-delocalization of the spin density at 21-carbaporphyrin.[8,9,34−36] This is in line with the ESR measurements which implicate the identical ground electronic state.

The ^{2}H NMR studies on **5** selectively deuterated at the 21-methyl group firmly confirmed a copper(II)−carbon(21) interaction. For the copper(II) complex (2-NCH$_3$-21-CD$_3$CTPP)Cu^{II}Cl the 21-CD$_3$ resonance is observed at −19.5 ppm (CH$_2$Cl$_2$, 293 K) indicating unpaired spin delocalization on the 21-CD$_3$ moiety which presumably requires the existence of Cu(II)-C(21) bond as a essential delocalization pathway (Figure 3, trace B). However the extent of delocalization and the sign of the 21-CD$_3$ isotropic shift are different in comparison with (2-NCH$_3$-

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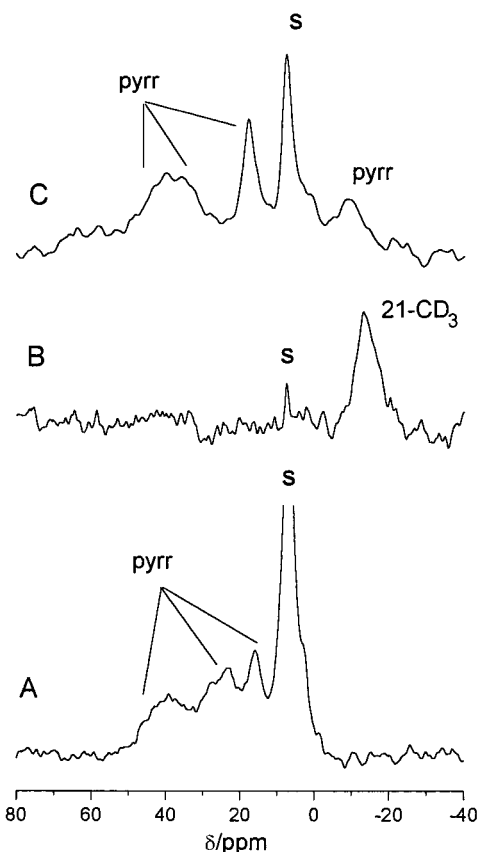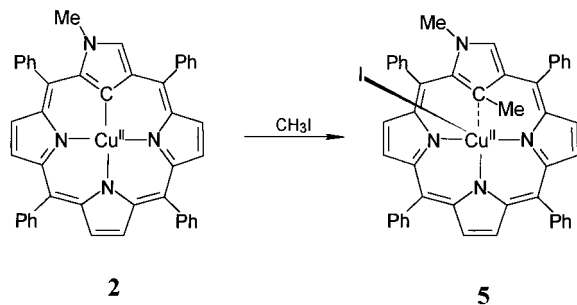
Figure 3. 46 MHz ^{2}H NMR spectra: (A) **1**, (CTPP-d_7)Cu^{II} (333 K, toluene); (B) **5**, (2-NCH$_3$-21-CD$_3$CTPP)Cu^{II}Cl (293 K, dichloromethane); (C) **5**, (2-NCH$_3$-21-CH$_3$CTPP-d_7)Cu^{II}Cl (293 K, dichloromethane). Pyrr denotes pyrrole resonances; s = solvent peaks.

Scheme 3

Chart 1

21-CD$_3$CTPP)Ni^{II}Cl which may result from the different electronic structure in both cases.[9]

Of particular importance is the observation that **5** can be obtained by an independent route, namely by methylation of (2-NCH$_3$CTPP)Cu^{II} with methyl iodide (298 K). The reaction is facilitated by a presence of 2,4,6-collidine (Scheme 3).

No such reaction has been observed for (2-NCH$_3$CTPPH)-Cu^{II}X, CTPPH$_2$ or 2-NCH$_3$CTPPH.[4,9] This reactivity resembles that of (CTPP)Ni^{II} or (2-NCH$_3$CTPP)Ni^{II}.[9] A feasible reaction mechanism involves the oxidative addition of the methyl cation to the carbaporphyrin C(21) atom that is activated due to the copper(II)$-\sigma$-pyrrole carbon(21) coordination. Similar reactivity of (2-NCH$_3$CTPP)Cu^{II} and (2-NCH$_3$CTPP)Ni^{II} implies existence of a σ-carbanion to copper(II) bond as such a structure seems to be a prerequisite for a methylation step.[9]

Protonation Modes of Nickel(II) and Zinc(II) Inverted Porphyrins. The variety of coordination modes that can be adopted by the inner carbon atom of copper(II) inverted
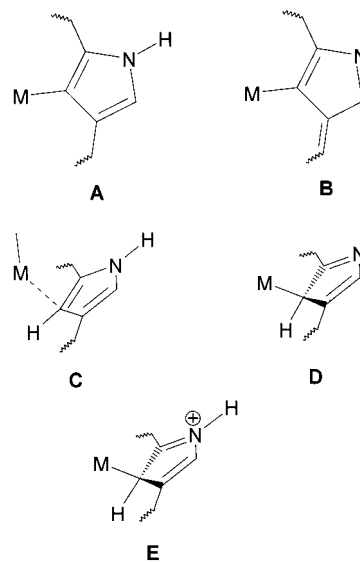
porphyrin (see Chart 1) and its methylated derivatives prompted us to a closer examination of protonation of carbaporphyrinoids and their complexes.

Protonation of the inner carbon atom of a free base has been described for the dicarbaporphyrin derivative.[37] Recently, protonation of nickel(II) complexes of heptaalkylated inverted porphyrins has been reported.[6] Here, we have turned our attention to the well-defined, diamagnetic nickel(II) complexes, presumably structural analogues of (CTPP)Cu^{II} and (2-NCH$_3$-CTPP)Cu^{II}, i.e., (CTPP)Ni^{II} and (2-NCH$_3$CTPP)Ni^{II}, where direct insight into the protonation mechanism and the structure of species formed could be achieved using NMR spectroscopy. Titrations of CDCl$_3$ solutions of these complexes with HCl, trifluoroacetic acid (TFA), or dichloroacetic acid (DCA), were monitored by ^{1}H NMR spectroscopy at 233 or 213 K, as all signals were broad at 293 K due to the fast chemical exchange between protonated and unprotonated complexes. The reversible spectral change upon TFA addition to (CTPP)Ni^{II} involves appearance of a new peak located at -3.10 ppm (Figure 4, trace A). The original ^{1}H NMR spectrum of (CTPP)Ni^{II} can be recovered by shaking the solution of the protonated complex with potassium carbonate or its solution in water. The new upfield resonance has been assigned to the 21-C*H* position based upon its peculiar chemical shift. Such a shift value is typical for protons located in the center of the aromatic carbaporphyrin.[1,2,6,9] The ^{1}H$-^{13}$C HMQC experiment has unambiguously demonstrated that this proton is directly linked to a carbon atom excluding possibility of the alternative NH assignment. The 21-H chemical shift does not depend on the acid used (the same value was observed for HCl, TFA, and DCA) or on the acid/complex molar ratio. On the other hand, these factors influenced the resonance position in the course of titration of nickel(II) inverted alkylated porphyrin complexes suggesting the formation of tight ionic pairs.[6] The 21-^{13}C*H* signal in the ^{1}H$-^{13}$C correlation spectrum of [(CTPPH)Ni^{II}]TFA appears at 31.9 ppm, a region which is typical for aliphatic carbon atoms. In fact, both CTPPH$_2$ and 2-NCH$_3$CTPPH, for which the inner 21-carbon atoms have sp^2 hybridization, 21-^{13}C*H* peaks appears in the low-field region of the spectra (99 and 105 ppm, respectively).[4] Similarly, the 21-^{13}C peak for the parent (CTPP)Ni^{II} complex is likely located

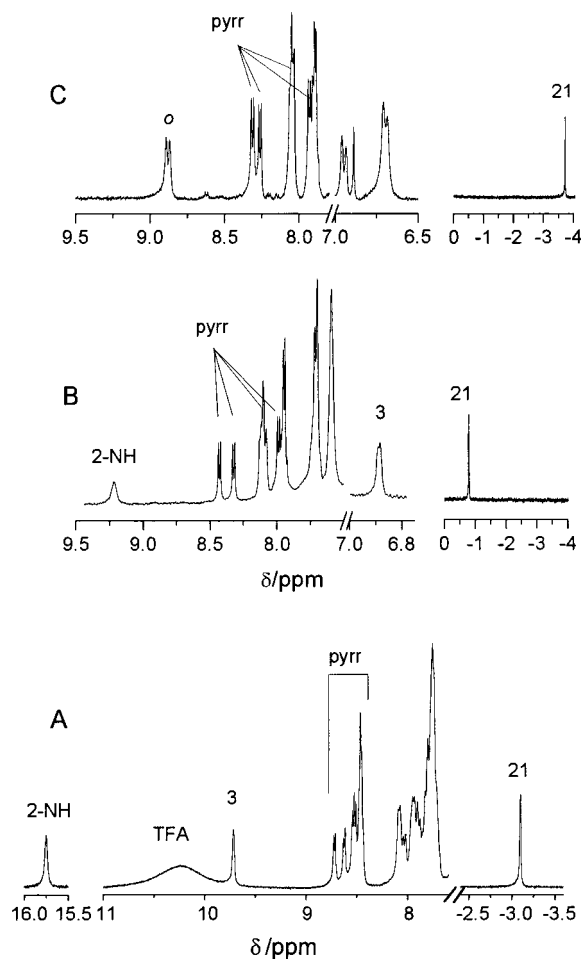(37) Lash, T. D.; Romanic, J. L.; Hayes, M. J.; Spence, J. D. *Chem. Commun.* **1999**, 819.

Figure 4. 300 MHz ^{1}H NMR spectra (chloroform-*d*) of (A) [(CTPPH)-Ni[II]]TFA (213 K); (B) (CTPPH)Zn[II]Cl (293 K), (C) (CTPPH)Zn[II]Cl after addition of CH₃ONa (293K). Peak labels follow systematic position numbering; regular pyrrole ring protons denoted as pyrr; *o* = ortho protons of *meso*-phenyl substituents

in the region of quaternary aromatic carbon atoms (120−150 ppm) since no ^{13}C signal has been observed between 20 and 120 ppm for this compound. Such a marked difference in the chemical shift between the trigonal, "aromatic" carbon atoms in CTPPH₂, 2-NCH₃CTPPH, and (CTPP)Ni[II] on one hand and that of 21-C*H* in [(CTPPH)Ni[II]]⁺ on the other hand suggests a profound alteration in geometry of the coordinated C(21) donor atoms upon protonation. Thus, pyramidal sp³ hybridization of this carbon atom has been proposed in [(CTPPH)Ni[II]]⁺. Meaningfully, we observe a similar chemical shift (30.8 ppm, 233 K, CDCl₃) for the coordinated 21-*C*CH₃ atom of the diamagnetic, (21-CH₃CTPP)Ni[II]. In this compound the methylated pyrrole is bound to nickel via a pyramidal C(21) carbon in the [1]*η*- fashion as determined by X-ray crystallography.[9]

The chemical shifts of other *β*-pyrrolic protons of protonated nickel(II) complexes are similar to that of CTPPH₂, its mono- and dication or (21-CH₃CTPP)Ni[II] indicating that aromaticity of the system is retained.[1,9] The low-field signal at 15.75 ppm seen for [(CTPPH)Ni[II]]⁺ has been assigned to the 2-NH since it shows scalar coupling to 3-H (9.72 ppm) and gives no crosspeak on the [1]H−[13]C correlation map. The diamagnetic character of [(CTPPH)Ni[II]]⁺ indicates square-planar arrangement of the chromophore and lack of any apical ligand despite the fact that both C(21) and N(2) positions are occupied by protons. The geometry of the 21-CCH₃ fragment is expected to change upon 2-N protonation from pyramidal (sp³ hybridization,

σ-coordination) to trigonal become side-on coordinated.[9] Such a peculiar coordination has been established for paramagnetic (2-NCH₃-21-CH₃CTPP)Ni[II]I by X-ray crystallography.[9]

The alternative coordination mode of inverted porphyrin in which 21-C remains protonated has been observed for the appropriate zinc(II) complexes. The ^{1}H NMR spectra demonstrate the upfield signals for both complexes (−0.81 ppm for (CTPPH)Zn[II]Cl, −0.63 ppm for (2-NCH₃CTPPH)Zn[II]Cl) which were attributed to the 21-C*H* (Figure 4, trace B). Addition of strong base (CH₃ONa, NaOH/H₂O) causes only minor changes in the spectrum of (2-NCH₃CTPPH)Zn[II]Cl, likely due to the axial ligand exchange. However in the case of (CTPPH)Zn[II]Cl the deprotonation of the outer nitrogen with a strong base is evident since the relatively broad low-field NH signal (9.3 ppm) disappears upon the base addition. The 21-C*H* signal is still present but shifts to −3.7 ppm (Figure 4, trace C). Apparently the zinc(II) cation has less tendency to replace 21-H and to form a zinc(II)−carbon(21) bond comparable to nickel(II) and copper-(II), respectively. Significantly, the 21-[13]C*H* resonance of (CTPPH)Zn[II]Cl has been detected at 80 ppm in the [1]H−[13]C correlation spectrum, i.e., in a region, which is typical of sp² hybridization. The ^{13}C chemical shift of C(21) provides the structurally important piece of information indicating the side-on localization of the zinc(II) ion with respect to the inverted pyrrole ring.

Considering the substitution pattern of the inverted pyrrole ring in the series (CTPPH)Cu[II]Cl, (2-NCH₃CTPPH)Cu[II]Cl and (2-NCH₃-21-CH₃CTPP)Cu[II]Cl, we suggest similar molecular structure as that found for (2-NCH₃-21-CH₃CTPP)Ni[II]I, where the methylated pyrrole is bound to the nickel in the *η*[1]-fashion but the coordinating C(21) carbon atom preserves trigonal geometry.[9] Thus a coordination mode can be common for the five-coordinate Ni[II], Zn[II], and Cu[II] complexes provided that two protons or two methyl groups are attached simultaneously to both external nitrogen N(2) and internal C(21) carbon (forms **3b** and **4b** in Scheme 2). Likely four-coordinate [(CTPPH)-Cu[II]]⁺ and [(2-NCH₃CTPP)Cu[II]]⁺ formed by axial ligand dissociation from **3b** or **4b**, can adopt a structure analogous to that detected for [(CTPP)Ni[II]]⁺ (forms **3a** and **4a** in Scheme 2). We have also noticed that the ionic radius of the central metal ion may determine the coordination geometry of C(21). The diamagnetic nickel(II) ion with an empty $d_{x^2−y^2}$ orbital will match the smaller cavity created by the sp³ − hybridized C(21) carbon.[9] The partially (Ni[II] or Cu[II]) or fully occupied (Zn[II]) $d_{x^2−y^2}$ orbital will favor the side on geometry allowing for the longer M[II]−N and M[II]−C bond distances.

Electrochemical Investigation of Copper(II) Inverted Porphyrins. The redox properties of copper(II) inverted porphyrins were studied by the cyclic and differential pulse voltammetry. (CTPP)Cu[II] (**1**) and (2-NCH₃CTPP)Cu[II] (**2**) gave a similar electrochemical response showing two quasi-reversible redox couples, each due to one-electron oxidation and reduction (Figure 5, trace B). The half-wave potentials $E_{1/2}$(3) (Table 2) indicate a facile metal-centered oxidation of **1** and **2**. The oxidative potential values of 390 and 343 mV for the Cu[III]/Cu[II] process found for **1** and **2**, respectively, are significantly lower than those observed for the analogous nickel(II) complexes[8] (685 mV vs SCE, ΔE_{pp}= 69 mV for (CTPP)Ni[II], THF, TBAP). Thus the thermodynamic stability of trivalent copper complexes should exceed that of the corresponding nickel(III) inverted porphyrin species.[8] Oxidation of (2-NCH₃CTPPH)Cu[II]Cl (**4**−Cl) is significantly less favorable compared to oxidation of **1** or **2**.
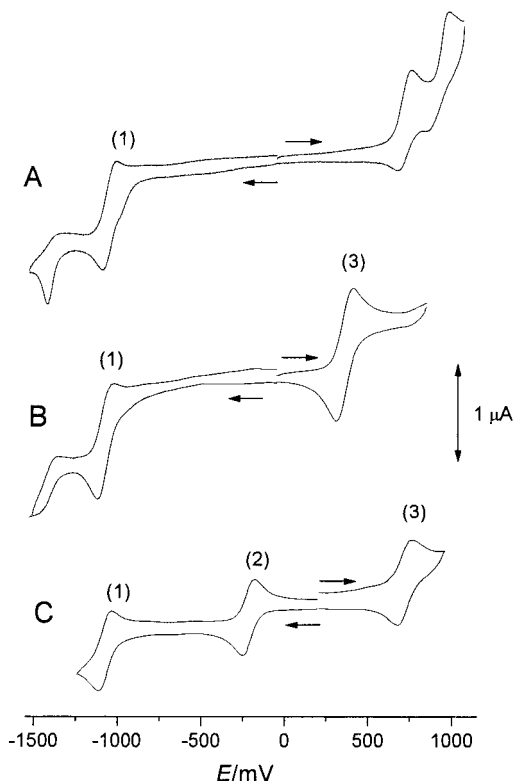
Figure 5. Cyclic voltammograms of (A) 2-NCH$_3$CTPPH; (B) (2-NCH$_3$-CTPP)Cu^{II} (**2**); (C) (2-NCH$_3$-21-CH$_3$CTPP)Cu^{II}Cl (**5**). The potential scan rate 100 mV s^{-1}. All potentials are given vs SCE. All measurements have been carried out in 0.1 M TBAP/THF at 293 K.

Titration of solutions of **1** or **2** with TFA resulted in a positive shift of the couple (3) in Figure 5 with the final $\Delta E_{1/2}(3) = 120$ mV. Stirring the solution of **1** or **2** after titration with the solid potassium carbonate slowly reverses the process and the addition of 2,4,6-collidine causes an instantaneous return of the redox couple potential to its original position. The potential of the couple (3), Figure 5 for **5** is about 300 mV more positive in comparison to the respective potentials of **1** or **2,** indicating that oxidation of **5** is less favorable. The value of $E_{1/2}(3)$ for **5** suggests a ligand-centered oxidation, since a quasi-reversible redox couple at 610 mV (THF, TBAP) has been observed for the 2-NCH$_3$-21-CH$_3$CTPPH free base.

The +1 oxidation state of copper is much less accessible for **1** or **2** than for **5**. All systems under study show a quasi-reversible couple near −1000 mV that can be accounted for by a ligand- rather than metal-centered reduction (Figure 5). In fact CTPPH$_2$ in dichloromethane solution[10] as well as 2-NCH$_3$-CTPPH (Figure 5, trace A) and 2-NCH$_3$-21-CH$_3$CTPPH free bases in THF give a redox couple with a potential close to −1000 mV vs SCE (−1046 mV, $\Delta E_{pp} = 75$ mV for 2-NCH$_3$-CTPPH and −932 mV, $\Delta E_{pp} = 80$ mV for 2-NCH$_3$-21-CH$_3$-CTPPH). In the series **1**, **2**, and **5**, only the dimethylated homologue **5** shows a couple (2) that can be attributed to the Cu^{II}/Cu^{I} transformation (Figure 5, trace C). The facile reduction of **5** is consistent with the monoanionic character of the dimethylated ligand.

Conclusion. The present work offers the spectroscopic evidence for stabilization of unusual organocopper(II) species via the very efficient protection of the copper(II)−carbon bond by encapsulating the coordinated copper(II) center in the coordination core of 2-aza-21-carbaporphyrin (NNNC) or related methylated macrocycles. As a result of steric constraints imposed by the ligand geometry, the C(21) carbon creates two distinctly different types of the copper(II)−carbon(21) bond. Its nature can be clearly exemplified by two methylated derivatives, i.e., (2-NCH$_3$CTPP)Cu^{II} where the equatorial macrocycle acts as an sp^2 σ-carboanion and (2-NCH$_3$-21-CH$_3$CTPP)Cu^{II}Cl where the methylated pyrrole seems to be bound to the copper in the η^1-fashion but the coordinating C(21) carbon atom preserves trigonal geometry. Coordination of carbon(21) to copper(II) in (2-NCH$_3$CTPP)Cu^{II} allows for the remarkable addition of HX or methylation both centered on the Cu(II)−C(21) moiety.

Experimental Section

Materials. Inverted porphyrin (CTPPH$_2$) and its methylated derivatives (2-NCH$_3$CTPPH, 2-NCH$_3$-21-CH$_3$CTPPH) as well as its nickel-(II) complexes were synthesized as described before.[1,4,9] Solvents used in syntheses and measurements were purified by standard methods except CDCl$_3$ (CIL or Dr. Glaser) used in ^{1}H NMR that was deacidified by passing down a basic alumina column and used without further purification. THF, toluene, and dichloromethane were degassed by freezing−pumping−thawing method and stored in the dry glovebox. Trifluoroacetic and dichloroacetic acids (Aldrich) were used as received.

Instrumentation. EPR spectra were recorded on the Bruker ESP 300 spectrometer operating with X-band equipped with a ER 035M gaussmeter and a HP 53550B microwave frequency counter. The spectra were simulated using a SYMRO program described earlier.[34] NMR spectra were recorded on the Bruker AMX 300 spectrometer. In each case spectra were referenced with residual signal of the solvent. The 2D experiments (^{1}H COSY and ^{1}H−^{13}C HMQC) were performed using standard software of the Bruker pulse program library. UV−vis spectra were recorded on the Hewlett-Packard 8435 diode-array spectrophotometer. The mass spectra were obtained on the AMD-604 spectrometer using EI and LSIMS ionization techniques or on the Finnigan MAT TSQ 700 spectrometer by means of ESI method. The electrochemical measurements were performed on the EA9C Multifunctional Electrochemical Analyzer using platinum or glassy-carbon disk as a working electrode and platinum wire for the auxiliary electrode. The saturated calomel or silver chloride electrodes were used as the reference electrodes and they was separated from the bulk solution by a glassy diaphragm connected to a bridge filled with the electrolyte solution.

Syntheses. All copper(II) insertions were carried out in the inert atmosphere of the MBraun glovebox using degassed solvents.

2-Aza-5,10,15,20-tetraphenyl-21-carbaporphyrinatocopper(II), (CTPP)Cu^{II} (1). 2-Aza-5,10,15,20-tetraphenyl-21-carbaporphyrin (50 mg, 80 mmol) was dissolved in THF (20 mL) and excess (100 mg) of copper acetate hydrate (POCh) was added as a THF solution (30 mL). The solution color changed immediately from red-brown to brown-green. The solution was allowed to stir for 5 h, and then the solvent was removed by reduced pressure. The solid was extracted with toluene with three 10 mL portions of the solvent. The extract was filtered, and the solution volume was reduced to about 10 mL. Addition of hexane resulted in appearance of brown precipitate that was dried in vacuo. Yield: 40 mg, 70%. UV−vis (CH$_2$Cl$_2$), λ/nm (log ϵ/cm^{-1} mol^{-1} dm^{-3}): 331(4.270), 388(4.377), 432sh, 451(4.758), 542(3.834), 588sh, 680(3.680), 739(3.753). MS-ESI(+): 676 (100%, [M + 1]$^+$), HRMS-LSIMS(+):

Table 2. Redox Parameters for Copper(II) Inverted Porphyrins

complex^a	$E_{1/2}(1)$ (mV)	$\Delta E_{pp}(1)$ (mV)	$E_{1/2}(2)$ (mV)	$\Delta E_{pp}(2)$ (mV)	$E_{1/2}(3)$ (mV)	$\Delta E_{pp}(3)$ (mV)
(CTPP)Cu (**1**)	−1070	68			390	84
(2-NCH$_3$-CTPP)Cu (**2**)	−1087	66			343	62
(2-NCH$_3$CTPPH)CuCl (**4**-Cl)	−1098	96			563	96
(2-NCH$_3$-21-CH$_3$CTPP)CuCl (**5**)	−1092	85	−224	70	713	78

^{a} THF solutions, 0.1 M TBAP. All potentials are given vs SCE.

675.16315, calculated for $C_{44}H_{28}N_4Cu$, 675.16101. Anal. Calcd for $C_{44}H_{28}N_4Cu\cdot2H_2O$: C, 74.19; H, 4.21; N, 7.88. Found: C, 74.47; H, 4.65; N, 7.44.

The same synthetic procedure was applied in the case of $(CTPP)^{63}Cu$ containing 98% of copper-63 isotope, coming out with $^{63}Cu(CH_3COO)_2$.

The complex containing porphyrin deuterated in all β-pyrrolic positions (1-d_7) was obtained in the same manner starting from the $CTPPH_2$-d_7 ligand that was obtained as described previously.[9]

2-Aza-2-methyl-5,10,15,20-tetraphenyl-21-carbaporphyrinato-copper(II), (2-NCH$_3$CTPP)Cu^{II} (2). Compound **2** was obtained in the same way as **1** starting from 50 mg of 2-aza-2-methyl-5,10,15,20-tetraphenyl-21-carbaporphyrin (2-NCH$_3$CTPPH). In this case mixing of the ligand with the metal salt resulted in a rapid color change from the grass-green to olive. Yield: 46 mg (80%). UV–vis (CH$_2$Cl$_2$), λ/nm (log ϵ/cm^{-1} mol^{-1} dm^{-3}): 332(4.181), 389(4.401), 432sh, 454(4.796), 543(3.704), 587(3.494), 682(3.680), 740(3.770). MS-EI (70 eV): 689.2 (100%, M − 1). Anal. Calcd for $C_{45}H_{30}N_4Cu\cdot2H_2O$: C, 74.41; H, 4.72; N, 7.71. Found: C, 74.84; H, 5.19; N, 7.44.

2-Aza-2-methyl-5,10,15,20-tetraphenyl-21-carbaporphyrinato-copper(II) Chloride, (2-NCH$_3$CTPPH)Cu^{II}Cl (4-Cl). Compound **4**-Cl was obtained by refluxing of 2-NCH$_3$CTPPH (30 mg, 48 mmol) with an excess of CuCl$_2$·2H$_2$O (30 mg) in THF for 1 h. After that time solvent was removed, and then toluene was applied to extract a green complex that precipitated after solvent volume reduction and addition of hexane. Yield: 19 mg (52%). UV–vis (CH$_2$Cl$_2$), λ/nm (log ϵ/cm^{-1} mol^{-1} dm^{-3}): 320(4.320), 415sh, 449(4.398), 472sh, 614(3.800), 670(3.760), 828(3.508). MS-LSIMS(+): 691 (10%, [M − Cl]$^+$). HRMS-ESI: 690.1823, calculated for $C_{45}H_{31}N_4Cu$, 690.1845. Anal. Calcd for $C_{45}H_{31}N_4CuCl\cdot H_2O$: C, 72.43; H, 4.16; N, 7.50. Found: C, 72.24; H, 4.19; N, 7.44.

2-Aza-2-methyl-5,10,15,20-tetraphenyl-21-methyl-21-carbapor-phyrinatocopper(II) Chloride, (2-NCH$_3$-21-CH$_3$CTPP)Cu^{II}Cl (5). Compound **5** was obtained on the same way as **4** starting from 2-aza-2-methyl-5,10,15,20-tetraphenyl-21-methyl-21-carbaporphyrin (2-NCH$_3$-21-CH$_3$CTPPH) (10 mg, 15.5 mmol). Yield: 8 mg (69%). UV–vis (CH$_2$Cl$_2$), λ/nm (log ϵ/cm^{-1} mol^{-1} dm^{-3}): 382(4.24), 432(4.29), 638(3.61), 731(3.61), 814(3.65). MS-LSIMS(+): 704 (20%, [M − Cl]$^+$). HRMS-LSIMS: 704.20335, calculated for $C_{46}H_{33}N_4Cu$, 704.20013. The same mass spectrometry results were obtained for the product of reaction of **2** (10 mg) in 20 mL of dichloromethane with an excess (100 mg) of methyl iodide after 7 days of stirring in the darkness. The EPR spectral characteristic indicated a mixture of products (presumably containing iodide and chloride axial ligands) that was converted to the chloride by addition of [TBA]Cl.

The complex containing porphyrin deuterated in all β-pyrrolic positions ((2-NCH$_3$-21-CH$_3$CTPP)Cu^{II}Cl, **5**-d_7) was obtained in the same manner starting from the 2-NCH$_3$-21-CH$_3$CTPPH-d_7 ligand that was obtained as described previously.[9] Analogously, the complex containing selectively deuterated inner methyl group ((2-NCH$_3$-21-CD$_3$CTPP)Cu^{II}-Cl, **5**-d_3) was obtained coming out with 2-NCH$_3$-21-CD$_3$CTPPH that was prepared by demetalation of the appropriate nickel(II) complexes—a product of reaction of (2-NCH$_3$CTPP)Ni^{II} with CD$_3$I, as described earlier.[9]

2-Aza-5,10,15,20-tetraphenyl-21-carbaporphyrinatozinc(II) chloride, (CTPPH)Zn^{II}Cl, was obtained by mixing of CTPPH$_2$ (25 mg, 40 mmol) in dichloromethane with an excess of zinc acetate dihydrate (40 mg) in methanol. The color of the mixture turned green immediately after combining both solutions. The solvents were then removed, and the solid residue was extracted with dichloromethane and filtered. The filtrate was shaken with the saturated aqueous solution of sodium chloride and washed with water. Organic layer was then separated and evaporated to dryness. After redissolving of the solid in dichloromethane and filtration the dark green product was precipitated by addition of hexane to the filtrate. Yield: 17 mg (60%). MS-LSIMS(+): 677 (30%, [M − Cl]$^+$). HRMS-ESI: 677.1670, calculated for $C_{44}H_{29}N_4Zn$, 677.1684. ^{1}H NMR (300 MHz, CDCl$_3$, 293 K): 9.22 (b, 1*H*, 2-NH), 8.44 (d, J_{AB} = 4.8 Hz, 1*H*), 8.33 (d, J_{AB} = 5.2 Hz, 1*H*), 8.14−8.10 (m, 4*H*), 7.99 (d, J_{AB} = 5.2 Hz, 1*H*), 7.98−7.93 (m, 4*H*), 7.73−7.70 (m, 6*H*), 7.60−7.59 (m, 6*H*), 6.91 (d, J = 1.5 Hz, 1*H*, 3-H), −0.81 (d, J = 1.5 Hz, 1*H*, 21-H).

2-Aza-2-methyl-5,10,15,20-tetraphenyl-21-carbaporphyrina-tozinc chloride, (2-NCH$_3$CTPPH)Zn^{II}Cl, was obtained on the same way as (CTPPH)Zn^{II}Cl starting from 2-NCH$_3$CTPPH (20 mg, 30 mmol). Yield: 15 mg (70%). MS-LSIMS(+): 692 (10%, [M − Cl]$^+$), HRMS-ESI: 691.1854, calculated for $C_{45}H_{31}N_4Zn$, 691.1840. ^{1}H NMR (300 MHz, CDCl$_3$, 293 K): 8.32 (d, J_{AB} = 4.8 Hz, 1*H*), 8.26 (d, J_{AB} = 5.2 Hz, 1*H*), 8.14−8.08 (m, 4*H*), 7.83−7.79 (m, 4*H*), 7.76−7.66 (m, 8*H*), 7.57 (m, 8*H*), 6.22 (d, ^4J = 1.1 Hz, 1*H*, 3-H), 3.21 (s, 3*H*, 2-NCH$_3$), −0.62 (d, J = 1.1 Hz, 1*H*, 21-H).