Reactions of Nickel(II) 2,21-Dimethyl-2-aza-21-carbaporphyrin with Phenyl Grignard Reagents, Phenyllithium, and *n*-Butyllithium

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Addition of a phenyl Grignard reagent to a toluene solution of the nickel(II) chloride complex of a dimethylated inverted porphyrin, $(2\text{-NCH}_3\text{-}21\text{-CH}_3\text{CTPP})\text{Ni}^{II}\text{Cl}$ (**1**), at 203 K results in the formation of a rare paramagnetic (σ-phenyl)nickel(II) species, $(2\text{-NCH}_3\text{-}21\text{-CH}_3\text{CTPP})\text{Ni}^{II}\text{Ph}$ (**2**). The coordination of the σ-phenyl in **2** is determined by a unique pattern of three σ-phenyl resonances (ortho 375.0 ppm; meta 108.94 ppm; para 35.68 ppm (at 283 K)) in the ^{1}H NMR and ^{2}H NMR spectra. The (σ-phenyl)nickel(II) compound **2** is in the high-spin ground electronic state $(d_{xy})^2(d_{xz})^2(d_{yz})^2(d_{z^2})^1(d_{x^2-y^2})^1$, as confirmed by similarity of the NMR spectra of the equatorial ligand in **1** and **2**. Titration of **1** with phenyllithium produces $(2\text{-NCH}_3\text{-}21\text{-CH}_3\text{CTPP})\text{Ni}^{II}\text{Ph}$ (**2**). One-electron reduction with excess PhLi yields $[(2\text{-NCH}_3\text{-}21\text{-CH}_3\text{CTPP})\text{Ni}^{II}\text{Ph}]^-$ (**3**), which can be also generated by independent routes, e.g., by reduction of $(2\text{-NCH}_3\text{-}21\text{-CH}_3\text{CTPP})\text{Ni}^{II}\text{Ph}$ using lithium triethylborohydride or tetrabutylammonium borohydride. The spectroscopic data indicate that $(2\text{-NCH}_3\text{-}21\text{-CH}_3\text{CTPP})\text{Ni}^{II}\text{Ph}$ (**2**) undergoes one-electron reduction without a substantial disruption of the molecular geometry. The presence of two paramagnetic centers in **3**, i.e., the high-spin nickel(II) and the carbaporphyrin anion radical, produces remarkable variations in a spectral patterns, such as the upfield and downfield positions of pyrrole resonances (103.78, 96.66, −25.35, −50.97, −92.15, −114.83 ppm (at 253 K)) and sign alternations of the meso-phenyl resonances (ortho −77.81, −79.34 ppm; meta 48.77, 48.04 ppm; para −85.65, −86.46 ppm (at 253 K)). A single species, **4**, is detected in the ^{1}H NMR titration of **1** with *n*-butyllithium. The formation of one- or two-electron-reduced species, $[(2\text{-NCH}_3\text{-}21\text{-CH}_3\text{CTPP})\text{NiBu}]^-$ or $[(2\text{-NCH}_3\text{-}21\text{-CH}_3\text{CTPP})\text{NiBu}]^{2-}$, respectively, is considered to account for the spectroscopic properties of **4** (pyrrole 17.33, 15.45, −5.79, −7.74, −14.62, −58.14 ppm; 21-CH$_3$ 3 ppm (at 203 K)). The temperature dependence of the hyperfine shifts of **4** demonstrates pronounced anti-Curie behavior, interpreted in terms of a temperature-dependent spin equilibrium between diamagnetic and paramagnetic states with diamagnetic properties approached as the temperature is lowered. Warming of **2**−**4** results in complete decomposition via homolytic/heterolytic cleavage of an axial nickel−apical carbon bond. In the case of **2** or **3**, the process yields a mixture of two compounds, **5** and **6**, which are detected by EPR spectroscopy, demonstrating the anisotropy of the **g** tensor (**5**, $g_1 = 2.237$, $g_2 = 2.092$, $g_3 = 2.090$; **6**, $g_1 = 2.115$, $g_2 = 2.030$, $g_3 = 1.940$ (in frozen toluene solution at 77 K)).

Introduction

Interchange of a nitrogen and a β-methine group in a pyrrole of 5,10,15,20-tetraphenylporphyrin (TPPH$_2$) results in the creation of the porphyrin-like skeleton 5,10,15,20-tetraphenyl-2-aza-21-carbaporphyrin (21-CTPPH$_2$, inverted tetraphenylporphyrin) although with fundamentally changed electronic and coordination properties.[1,2] A peralkylated, meso-unsubstituted inverted porphyrin has been synthesized as well.[3,4] The inverted porphyrin belongs to a larger group of recently emerged porphyrin isomers[5−9] although this particular molecule represents the only case where the pattern of the porphyrin framework is preserved.

A complementary and relevant area of porphyrin modification involves the replacement of one pyrrole ring by benzene,[10] semiquinone,[11,12] cycloheptatriene,[13,14] indene,[13,15] azulene,[16] cyclopentadiene,[17] an aliphatic bicyclic alkene,[18] and 2,4-linked thiophene[19] moieties. Such an approach provides a CH unit in the position of the pyrrole nitrogen, preserving the (N,NH,NH,CH) central core as a common structural denominator of carbaporphyrin-like macrocycles. 2-Aza-21-carba-23-oxaporphyrin and 2-aza-21-carba-23-thiaporphyrin, i.e., isomers of 21-oxaporphyrin and 21-thiaporphyrin, combine features of both: inverted porphyrin and 21-heteroporphyrin,[20,21] forming definitely dif-

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ferent coordination cores, i.e., (N,CH,N,O) and (N,CH,NH,S). The recent dicarbaporphyrinoid synthesis by Lash et al. provides an important addition to the carbaporphyrinoid class of macrocycles.[22]

Taking advantage of the unusual reactivity of the nickel carbaporphyrin and of the 21-carbaporphyrin free base, we have extended the group of inverted porphyrins with the corresponding methylated derivatives 2-methyl-5,10,15,20-tetraphenyl-2-aza-21-carbaporphyrin (2-NCH$_3$CTPPH), 5,10,15,20-tetraphenyl-21-methyl-2-aza-21-carbaporphyrin (21-CH$_3$CTPPH$_2$), and 2,21-dimethyl-5,10,15,20-tetraphenyl-2-aza-21-carbaporphyrin (2-NCH$_3$-21-CH$_3$CTPPH).[23,24]
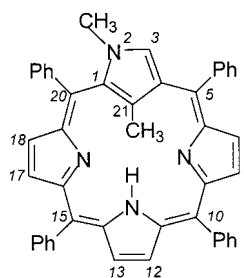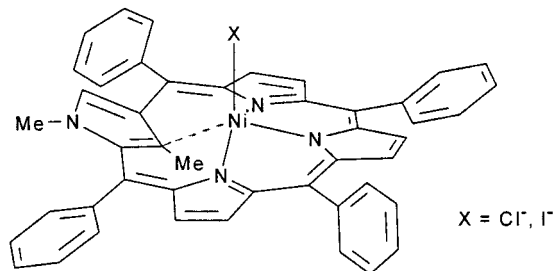

2-NCH$_3$-21-CH$_3$CTPPH

Carbaporphyrins and methylated carbaporphyrins act as mono- or dianionic ligands toward the nickel(II) and nickel(III) ions.[1,4,23-25] Thus one Ni−C and three Ni−N bonds are formed within the inverted tetrapyrrole macrocycle of (CTPP)Ni^{II} or (2-NCH$_3$CTPP)Ni^{II}. Both macrocycles act as four-coordinate dianionic ligands, enforcing the coordination of the pyrrole sp^2 carbon to nickel(II).[1,23] In the (21-CH$_3$CTPP)Ni^{II} case, the nickel(II) is four-coordinate with bonds to three pyrrole nitrogens and the pyrrole carbon.[24] The methylated pyrrole is bound to the nickel via a pyramidal carbon in an η^1 fashion. A similar mode of coordination can be expected in a nickel(II) inverted heptaalkyl porphyrin protonated at the C(21) carbon.[4] In the paramagnetic (2-NCH$_3$-21-CH$_3$CTPP)Ni^{II}I compound, the methylated pyrrole is linked to nickel in an η^1 fashion but the coordinating C(21) carbon preserves the features related to the trigonal sp^2 hybridization.[24] Furuta and co-workers have demonstrated that inverted porphyrins act as trianionic ligands, stabilizing the silver(III) cation.[26]

Paramagnetic organometallic nickel(II) complexes are rare and typically unstable, although with some remarkable exceptions.[24,27-30] Our contributions to the field, apart from (2-NCH$_3$-21-CH$_3$CTPP)Ni^{II}I,[24] include investigations on σ-phenyl coordination to the nickel(II) ion located within 21-heteroporphyrin (XTPPH; X = O, S, Se), N-methylporphyrin (N-

CH$_3$TPPH), and 21,23-dioxaporphyrin (O$_2$TPP) environments.[31-33] To search for novel paramagnetic organonickel(II) species bearing one or two σ-phenyls, we had previously investigated the reactions of (XTPP)Ni^{II}Cl or (O$_2$TPP)Ni^{II}Cl$_2$ with aryl Grignard reagents, anticipating replacement of one or both chloride ligands by σ-phenyl(s).[31-33] Despite thermal instability, the formation of paramagnetic organonickel(II) heteroporphyrins has been directly confirmed by means of ^{1}H NMR and ^{2}H NMR spectroscopy. Generally, the determined hyperfine shift patterns provided several useful and potentially unique probes for detecting (σ-phenyl)nickel heteroporphyrin derivatives.[31-39]

Here we report our efforts to obtain a novel class of paramagnetic organonickel complexes. We had observed that the structure of (2-NCH$_3$-21-CH$_3$CTPP)Ni^{II}I (**1**) contains the

X = Cl$^-$, I$^-$

1

essential features for coordination of σ-phenyl or σ-alkyl ligands in addition to the Ni^{II}−C(21) bond already forced by the equatorial macrocycle.[24] Consequently, we investigated the reactions of (2-NCH$_3$-21-CH$_3$CTPP)Ni^{II}Cl with aryl (alkyl) Grignard reagents and phenyl(alkyl)lithium, anticipating replacement of the apical ligand by σ-phenyl (σ-alkyl), to yield paramagnetic (2-NCH$_3$-21-CH$_3$CTPP)Ni^{II}R complexes, containing both equatorial and apical Ni^{II}−carbon bonds. The reactivity of these new organometallic species has been a matter of our interest as well.

Results and Discussion

General Procedures. Additions of the aryl Grignard reagents PhMgBr and (Ph-d_5)MgBr, butyllithium, and phenyllithium to toluene-d_8 solutions (203 K) of (2-NCH$_3$-21-CH$_3$CTPP)Ni^{II}Cl (**1**) resulted in the formation of a variety of paramagnetic organonickel species, which were detected and subsequently characterized by ^{1}H and ^{2}H NMR spectroscopy. The NMR resonance assignments are based on relative intensities, line width analysis, and site-specific deuteration using the following derivatives of (2-NCH$_3$-21-CH$_3$CTPP)Ni^{II}Cl: (2-NCD$_3$-21-CD$_3$CTPP)Ni^{II}Cl, (2-NCH$_3$-21-CD$_3$CTPP)Ni^{II}Cl, (2-NCH$_3$-21-CH$_3$CTPP-d_7)Ni^{II}Cl (deuterated in all pyrrole β positions), and (2-NCH$_3$-21-CH$_3$CTPPH-d_{20})Ni^{II}Cl (deuterated in all positions
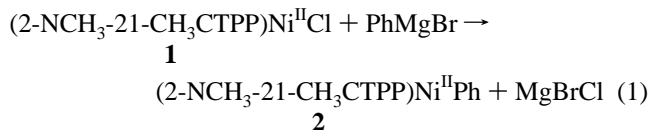
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of the meso-phenyl rings). In each case, the stoichiometry of the σ-phenyl adduct was unambiguously determined by a careful comparison of resonance intensities (integrated signal areas) assigned to the equatorial macrocycle and σ-phenyl (ortho, meta, and para) protons, respectively. The spectral patterns of the formed σ-phenyl complexes strongly depend on the ligand sources.

The half-wave potentials for the two one-electron reductions of (2-NCH$_3$-21-CH$_3$CTPP)Ni^{II}Cl, (1) -0.698 and (2) -0.970 V (vs SCE; THF solution, TBAP), are close to the corresponding reduction potentials found for nickel(II) heteroporphyrins.[39] Thus, the alternative reaction pathways of (2-NCH$_3$-21-CH$_3$CTPP)Ni^{II}Cl with aryl (alkyl) reagents may result in one- or two-electron reductions with or without a formation of a nickel−carbon bond and such a route will be included in our analysis. Alkyllithium, aryllithium, and Grignard reagents are known to act as one-electron-reducing reagents.[40−46] The reduction has been also demonstrated in several attempts to generate metalloporphyrins with metal−carbon bonds.[40,41,44−46]

Reactions with Phenyl Grignard Reagents. Titration of **1** with PhMgBr (toluene-d_8, 203 K) led to the substitution of one chloride ligand by the phenyl anion, yielding the complex (2-NCH$_3$-21-CH$_3$CTPP)Ni^{II}Ph (**2**) according to the reaction

$$(2\text{-NCH}_3\text{-}21\text{-CH}_3\text{CTPP})\text{Ni}^{II}\text{Cl} + \text{PhMgBr} \rightarrow$$
$$\mathbf{1}$$
$$(2\text{-NCH}_3\text{-}21\text{-CH}_3\text{CTPP})\text{Ni}^{II}\text{Ph} + \text{MgBrCl} \quad (1)$$
$$\mathbf{2}$$

The (2-NCH$_3$-21-CH$_3$CTPP)Ni^{II}Ph species **2** has been observed in the temperature range 203−283 K although substantial decomposition has been observed above 263 K. Representative NMR spectra are shown in Figure 1. The coordination of the apical σ-phenyl ligand has been unambiguously confirmed by the "fingerprint"-type downfield pattern of the three resonances in the ^{2}H NMR spectrum (ortho 375.0 ppm; meta 108.94 ppm; para 35.68 ppm (at 283 K)). The ^{1}H (^{2}H) NMR spectral characteristics and accordingly the electronic structure of **2** are similar to those determined for the analogous species which were formed in the course of PhMgBr(Cl) reactions with nickel(II) complexes of core-modified porphyrins, i.e., (NCH$_3$-TPP)Ni^{II}Ph, (OTPP)Ni^{II}Ph, (STPP)Ni^{II}Ph, (SeTPP)Ni^{II}Ph, and (O$_2$TPP)Ni^{II}(Ph)Cl.[31−33] The characteristic paramagnetic shifts are collected in Table 1, for the sake of comparison, with the respective shifts of the parent complex **1**.[24] Patterns of NMR spectra determined for (2-NCH$_3$-21-CH$_3$CTPP)Ni^{II}Cl (**1**), (2-NCH$_3$-21-CH$_3$CTPP)Ni^{II}I[24] (**1′**), and (2-NCH$_3$-21-CH$_3$CTPP)-Ni^{II}Ph (**2**) are similar, and observed differences reflect only the fine effects due to the axial coordination. It was previously shown for (2-NCH$_3$-21-CH$_3$CTPP)Ni^{II}I[24] (**1′**) that the nickel(II) ion is five-coordinated with equatorial bonds to three pyrrole nitrogen atoms and to the pyrrole C(21) carbon. The nickel is
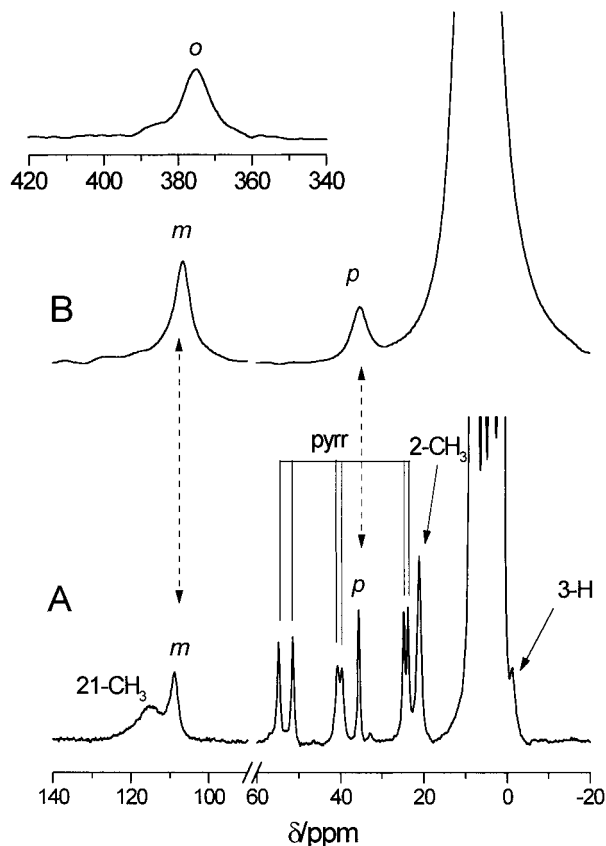
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Figure 1. NMR spectra of (σ-phenyl)nickel(II) dimethylated inverted porphyrin (2,21-dimethyl-5,10,15,20-tetraphenyl-2-aza-21-carbaporphyrin) complexes **2**: (A) (2-NCH$_3$-21-CH$_3$CTPP)Ni^{II}Ph, ^{1}H NMR; (B) (2-NCH$_3$-21-CH$_3$CTPP)Ni^{II}(Ph-d_5), ^{2}H NMR. Spectra were recorded in toluene solutions (A) C$_7$D$_8$ and (B) C$_7$H$_8$ at 283 K. Peak labels follow the systematic numbering of the carbaporphyrin ring or denote proton groups: pyrr, pyrrole; o, ortho, m, meta, and p, para phenyl protons (deuterons) of the σ-bonded phenyl ligand.

moved out from the three-nitrogen plane toward the iodo ligand. The 21-CH$_3$ group and iodide are located on the opposite sides of the macrocycle. The substituted pyrrole is bound to nickel in an η^1 fashion, but the coordinating C(21) atom preserves features related to trigonal sp^2 hybridization. On the basis of the paramagnetic shift similarity, one can presume that replacement of the chloro or iodo ligand by the σ-phenyl ligand in **2** preserves the basic structural features of **1** or **1′**.[24]

The Curie plots of the temperature dependence of the chemical shifts of the pyrrole and methyl resonances of (2-NCH$_3$-21-CH$_3$CTPP)Ni^{II}Ph (not shown), collected in a limited temperature range, demonstrate linear behaviors with extrapolated intercepts that do not correspond to the suitable diamagnetic references, e.g., (21-CH$_3$CTPP)Ni^{II} or the relevant carbaporphyrin.[24] Actually the deviations are a result of curvatures of $\delta = f(1/T)$ plots. These deviations, which are typical for nickel(II) heteroporphyrins, indicate small contributions from dipolar shifts due to the anisotropies of zero-field splittings.[24,31−35,39] Generally, one can conclude that the (σ-phenyl)nickel(II) derivative is in the high-spin state (d$_{xy}$)^2-(d$_{xz}$)^2(d$_{yz}$)^2(d$_{z^2}$)^1(d$_{x^2-y^2}$)^1. The spin transfer occurs via an interaction of the unpaired electron in the σ-symmetric Ni d$_{z^2}$ atomic orbital with the phenyl orbital of σ-symmetry. The large downfield σ-contact shifts of the apical phenyl provide the experimental evidence for such a description of the delocalization mechanism.

Particularly, the downfield shifts of pyrrole and *C(21)*-methyl resonances indicate a σ-delocalization of spin density. This

Table 1. Chemical Shifts of Nickel(II) Complexes of Inverted Porphyrins (ppm)

complex	pyrrole H	inverted pyrrole 2,3-H	N- or C-CH$_3$ H	axial ligand H
(2-NH-21-CH$_3$CTPP)Ni^{II}Cl[a]	58.06, 58.06, 52.40, 48.25,26.53, 24.86	2.04 (3-H), −23.07 (2-NH)	109.7 (21-CH$_3$)	
(2-NCH$_3$-21-CH$_3$CTPP)Ni^{II}Cl[a] (**1**)	59.62, 55.95,50.91, 49.33, 28.15, 27.16	−1.67	98.81 (21-CH$_3$), 28.30 (2-CH$_3$)	
(2-NCH$_3$-21-CH$_3$CTPP)Ni^{II}Ph[b] (**2**)	54.92, 51.52, 40.81, 39.75, 24.91, 23.89	−1.17	115.43 (21-CH$_3$), 21.19 (2-CH$_3$)	375.0 (*o*), 108.94 (*m*), 35.68 (*p*)
[(2-NCH$_3$-21-CH$_3$CTPP)Ni^{II}py]Cl[c]	81.07, 78.07, 67.48, 63.34, 36.38, 36.44	−8.53	157.70 (21-CH$_3$), 59.98 (2-CH$_3$)	215.18 (*o*), 71.18 (*m*), 20.28 (*p*)
[(2-NCH$_3$-21-CH$_3$CTPP)Ni^{II}Ph]$^{−}$ [d] (**3**)	103.78, 96.66, −25.35, −50.97, −92.15, −114.83		217.20 (21-CH$_3$), 86.80 (2-CH$_3$)	123.30 (*m*), 111.61 (*m*), 39.82 (*p*)
[(2-NCH$_3$-21-CH$_3$CTPP)NiBu]$^{n−}$ [e] (**4**)	14.95, 13.48, −3.45, −4.37, −10.16, −46.87		19.17 (2-CH$_3$), 3.32 (21-CH$_3$)	22.07, 21.36, 18.5, −21.91

[a] Chloroform-*d*, 293 K; data from ref 24. [b] Toluene-*d$_8$*, 283 K. [c] Toluene-*d$_8$*, 223 K. [d] Toluene-*d$_8$*, 253 K; the signals of meso-aryl protons were observed at 48.77 (2H, *m*), 48.06 (2H, *m*), −77.81 (2H, *o*), −79.34 (2H, *o*), −85.65 (1H, *p*), and −86.46 ppm (1H, *p*). [e] Toluene-*d$_8$*, 203 K.
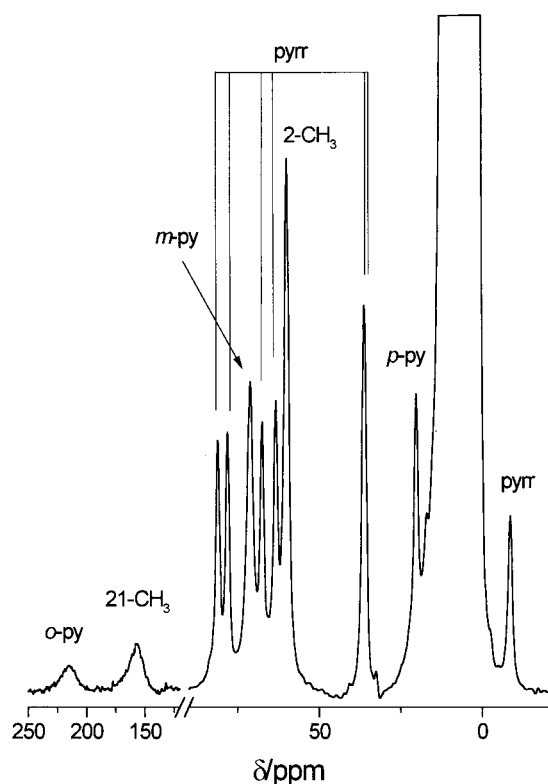

Figure 2. 300 MHz ^{1}H NMR spectrum of [(2-NCH$_3$-21-CH$_3$CTPP)-Ni^{II}(py)]$^+$ in toluene-*d$_8$* at 223 K. A total of 10 equiv of pyridine was added with respect to starting (2-NCH$_3$-21-CH$_3$CTPP)Ni^{II}Cl. Assignment of the dimethylated inverted porphyrin resonances is as in Figure 1; *o*-py, *m*-py, *p*-py = ortho, meta, para resonances of the pyridine ligand.

mechanism has been described previously in detail for **1**, and it is common for nickel core-modified systems.[24,31−39] The shift pattern of the carbaporphyrin equatorial ligand resembles that found for the [(2-NCH$_3$-21-CH$_3$CTPP)Ni^{II}(py)]$^+$ species, generated by titration of (2-NCH$_3$-21-CH$_3$CTPP)Ni^{II}Cl with pyridine, as shown in Figure 2 (toluene-*d$_8$*, 223 K):

$$(2\text{-NCH}_3\text{-}21\text{-CH}_3\text{CTPP})\text{Ni}^{II}\text{Cl} + \text{py} \rightleftharpoons$$

$$[(2\text{-NCH}_3\text{-}21\text{-CH}_3\text{CTPP})\text{Ni}^{II}(\text{py})]^+ + \text{Cl}^- \quad (2)$$
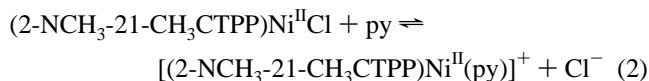
As expected the shift patterns of axially coordinated pyridine and the phenyl anion are alike, as both ligands are isoelectronic.[31]

Reactions with Phenyllithium. Titration of **1** with PhLi (toluene-*d$_8$*) carried out at 203 K resulted unexpectedly in a more
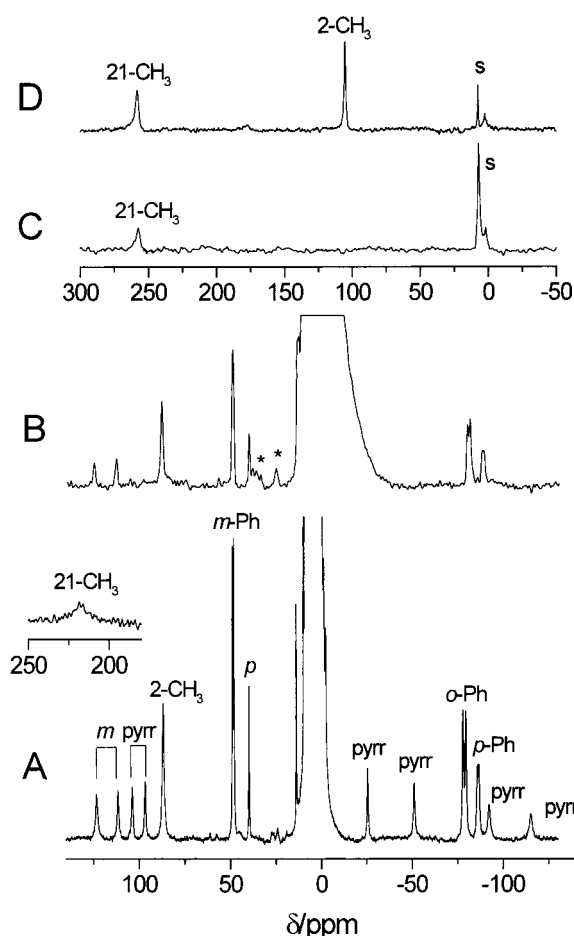

Figure 3. NMR spectra of **3**, formed by treating **1** with phenyllithium in toluene at 203 K: (A) [(2-NCH$_3$-21-CH$_3$CTPP)Ni^{II}Ph]$^−$, ^{1}H NMR, C$_7$D$_8$, 253 K; (B) [(2-NCH$_3$-21-CH$_3$CTPP-*d$_7$*)Ni^{II}Ph]$^−$, ^{1}H NMR, C$_7$D$_8$, 253 K; (C) [(2-NCH$_3$-21-CD$_3$CTPP)Ni^{II}Ph]$^−$, ^{2}H NMR, C$_7$H$_8$, 223 K; (D) [(2-NCD$_3$-21-CD$_3$CTPP)Ni^{II}Ph]$^−$, ^{2}H NMR, C$_7$H$_8$, 223 K. Assignment of the dimethylated inverted porphyrin resonances is as in Figure 1; *o*-Ph, *m*-Ph, *p*-Ph = resonances of strongly paramagnetic shifted meso-phenyl substituents of the dimethylated inverted porphyrin. The residual resonances of **6** are marked with asterisks.

complex ^{1}H NMR picture than that determined in the analogous experiment using PhMgBr. Initially, the ^{1}H NMR spectrum of (2-NCH$_3$-21-CH$_3$CTPP)Ni^{II}Ph (**2**) was accompanied by a well-defined set of paramagnetic shifted resonances corresponding to the novel compound **3**. Compound **3** forms exclusively when phenyllithium is used in excess (Figure 3). The ^{1}H NMR spectrum of **3** is different from that of any paramagnetic

nickel(II) porphyrin or heteroporphyrin.[24,31−39] On the basis of its unusual NMR features (vide infra), the second monophenyl adduct has been identified as the product of a one-electron reduction of **2**, i.e., [(2-NCH$_3$-21-CH$_3$CTPP)NiPh]$^-$ (**3**), formed in a two-step process:

$$(2\text{-NCH}_3\text{-}21\text{-CH}_3\text{CTPP})\text{Ni}^{II}\text{Cl} + \text{PhLi} \rightarrow$$
$$(2\text{-NCH}_3\text{-}21\text{-CH}_3\text{CTPP})\text{Ni}^{II}\text{Ph} + \text{LiCl} \quad (3)$$

$$(2\text{-NCH}_3\text{-}21\text{-CH}_3\text{CTPP})\text{Ni}^{II}\text{Ph} + \text{PhLi} \rightarrow$$
$$[(2\text{-NCH}_3\text{-}21\text{-CH}_3\text{CTPP})\text{Ni}^{II}\text{Ph}]\text{Li} + \text{Ph}^{\bullet} \quad (4)$$
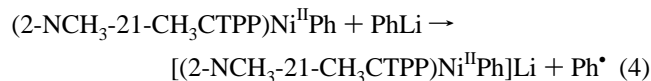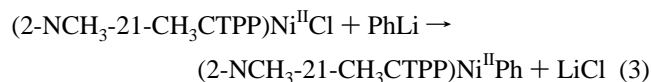
To verify that the conversion of **2** to **3** is exclusively a reduction, we demonstrated that **3** can been generated by independent routes. The ^{1}H NMR titration of **1** with PhMgBr (toluene-d_8, 203 K) to produce (2-NCH$_3$-21-CH$_3$CTPP)Ni^{II}Ph (**2**) may be followed by the addition of a reducing reagent such as lithium triethylborohydride or tetrabutylammonium borohydride. The observation that **3** can be generated using a combination of PhMgBr and tetrabutylammonium borohydride excludes any special role of the lithium cations in the stabilization of **3**.

The ^{1}H NMR spectrum of **3** (Figure 3, trace A) revealed six pyrrole resonances: two of them shifted downfield (103.78, 96.66 ppm) but four shifted remarkably upfield (−25.35, −50.97, −92.15, −114.83 ppm (at 253 K)). The seventh pyrrole resonance could not be located despite considerable effort. It was likely obscured by the signal of the solvent (heptane or THF) added with phenyllithium. The coordination of one σ-phenyl ligand has been unambiguously determined. The corresponding two meta resonances (123.30, 111.61 ppm) and one para resonance (39.08 ppm) have been assigned in the ^{1}H NMR spectrum (Figure 3, traces A and B). Their positions parallel those recognized as typical for apical coordination of σ-phenyl ligands in five-coordinate high-spin nickel(II) core-modified porphyrins,[31−33] including (2-NCH$_3$-21-CH$_3$CTPP)Ni^{II}Ph (**2**) (Table 1). For **3**, two meta resonances with intensities corresponding to one proton were observed rather than the expected single two-proton signal. The resolution of two σ-phenyl meta resonances for **3** in contrast to **2** must result from hindered rotation about the Ni−C bond that is slow on the NMR time scale. Most likely, the σ-phenyl ligand binds with its plane parallel to the N(2)−C(3) bond. Consequently, the carbaporphyrin asymmetry removes the intrinsic C_2 symmetry of the coordinated σ-phenyl, rendering the two meta protons and the two ortho protons inequivalent. Other orientations are less favorable because they may create a disadvantageous contact between the σ-phenyl ligand and the methylated pyrrole ring. This phenomenon, although feasible because of the identical symmetries of the equatorial macrocycles, has been observed neither for the related (2-NCH$_3$-21-CH$_3$CTPP)Ni^{II}Ph nor for [(2-NCH$_3$-21-CH$_3$CTPP)Ni^{II}(py)]$^+$ in the same temperature range. This reflects the difference in the dynamic behaviors related to the rotation with respect to the Ni−C$_{phenyl}$(N$_{pyridine}$) bond. Likely, one-electron reduction of **2** to generate **3** causes a structural rearrangement that increases this rotation barrier. A similar restriction of rotation was determined in the case of coordination of 4-methylimidazole by iron(III) *N*-methylporphyrin.[47]

The downfield broad resonance at 257.9 ppm (223 K) has been assigned to the 21-CH$_3$ group. This resonance appears in
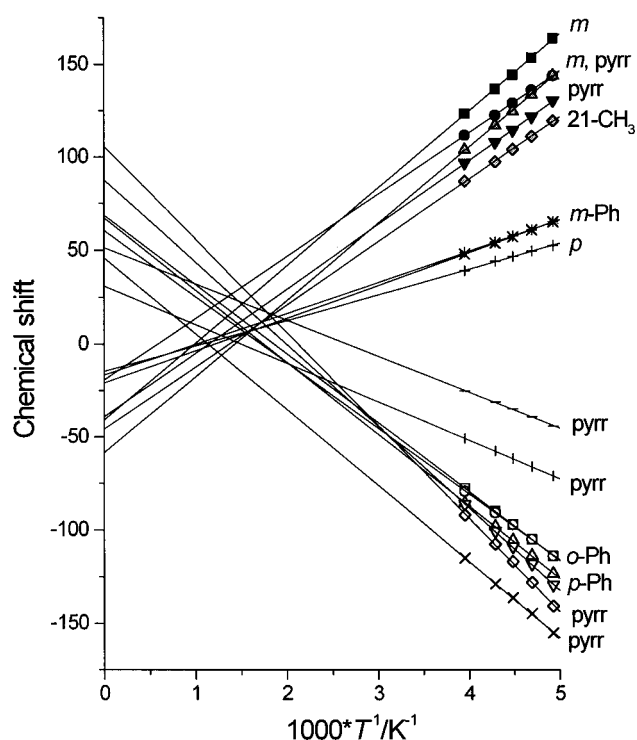
(47) Balch, A. L.; Cornman, C. R.; Latos-Grażyński, L.; Olmstead, M. M. *J. Am. Chem. Soc.* **1990**, *112*, 7552.

Figure 4. Plots of the chemical shifts versus $1/T$ for [(2-NCH$_3$-21-CH$_3$CTPP)Ni^{II}Ph]$^-$ (**3**) in toluene-d_8. Assignments of the resonances follow those in Figure 3.

the ^{2}H NMR spectrum of [(2-NCH$_3$-21-CD$_3$CTPP)NiPh]$^-$ (Figure 3, trace C). The 2-NCD$_3$ resonance is found at 104.8 ppm in the ^{2}H NMR spectrum of [(2-NCD$_3$-21-CD$_3$CTPP)Ni^{II}-Ph]$^-$ at 233 K (Figure 3, trace D). The remaining, paramagnetic shifted resonances of **3** shown in Figure 3 have been assigned to the meso-phenyls. The preliminary analysis, based on the C_1 geometry of **3**, requires four inequivalent meso-phenyls, each presenting one para, two meta, and two ortho proton resonances. The two ortho and the two meta protons on each of the meso-phenyl rings are inequivalent, since the porphyrin plane bears different substituents on the opposite faces and the rotation about the C$_{meso}$−C$_{phenyl}$ bond may be restricted. Since all meso-phenyl rings are structurally different and are exposed to different steric hindrances, it is anticipated that there will be some differences in their rates of rotation. Pairwise rotationally averaged features of ortho and meta phenyl resonances have been seen for two meso-phenyl rings. Two resonances of comparable line widths at 48.77 and 48.06 ppm have been observed, each demonstrating the intensity of two protons. These are assigned to the meso-phenyl meta protons. Two other meso-phenyl resonances (each revealing a two-proton intensity as well) have been identified at −77.81 and −79.34 ppm (253 K) and are assigned to the ortho protons originating from the same meso-phenyl rings. Finally, the remaining two resonances (each of one-proton intensity) at −85.65 and −86.46 ppm (253 K) are assigned to the corresponding para protons. The sign alternation of the meso-phenyl resonances and the sizes of the isotropic shifts indicate very large π-spin densities at two out of four carbaporphyrin meso positions. The resonances of the two other phenyls are located in the rather typical 19−9 ppm region for meso-phenyls of nickel(II) tetraphenylporphyrin derivatives.[31−39] At this stage, we cannot assign meso-phenyl resonances to the specific meso positions in the macrocyclic structure.

The Curie plots of the temperature dependence of the chemical shifts of the pyrrole and methyl resonances of **3** (Figure 4) demonstrate linear behaviors over the limited temperature

range that could be examined. The extrapolated intercepts do not correspond to the suitable diamagnetic references. The observed deviations from the Curie law resemble those seen for high-spin nickel(II) heteroporphyrins.[24,31−38]

The spectroscopic data reported here indicate that (2-NCH$_3$-21-CH$_3$CTPP)Ni^{II}Ph (**2**) undergoes a one-electron reduction by phenyllithium without a substantial disruption of the molecular geometry. The ^{1}H NMR data for **3** show a number of remarkable features that must arise from its unusual molecular and electronic structures. With regard to molecular structure, the observation of paramagnetic shifted σ-phenyl resonances is of particular importance. It is consistent with the presence of a five-coordinate high-spin nickel(II) ion apically coordinated by a σ-phenyl.[31−33] As a matter of fact, the isotropic shift of the σ-phenyl can be used here as the definitive and selective probe of the high-spin electronic state of the nickel(II) ion for the composite electronic structure of **3**. The large downfield shift of the 21-CH$_3$ group (Table 1) implies a preservation of the equatorial nickel(II)−carbon(21) bond.

^{1}H NMR spectroscopy has been shown to be the definitive method for characterizing paramagnetic metalloporphyrins.[48−51] The paramagnetic shifts of porphyrins and porphyrin substituents are sensitive to the electronic structure of metalloporphyrins. Consequently, similar spectra can be observed independently of the metal ion coordinated by a porphyrin, showing the similarity of the ground electronic states. Two classes of metalloporphyrins may be relevant models expected to share spectroscopic features with [(2-NCH$_3$-21-CH$_3$CTPP)NiPh]$^-$ (**3**) and [(2-NCH$_3$-21-CH$_3$CTPP)Ni(n-Bu)]$^-$ (**4**). These are (a) iron porphyrin π-cation radicals[51−57] and (b) two-electron-reduced high- or low-spin iron(III) porphyrins.[50,58−61] In the second case, the electronic structure can be described as the resonance hybrid of two extreme canonical structures, i.e., an iron(I) porphyrin and an iron(II) porphyrin π-anion radical. Apparently two paramagnetic centers in the metalloporphyrin are required to produce some of the NMR features detected for **3** and **4**. Furthermore, both the large spread of meso-phenyl resonances and the shift alternation of the pyrrole resonance signs have precedent, particularly in systems with intrinsic asymmetries of porphyrin skeletons.[62−64] Similarly, the pertinent couplings between high-spin nickel(II) ions and unpaired electrons local-

ized on a porphyrin π-cation radical and on an oxophlorin radical were previously reported.[65,66] Consequently, we have concluded that the observed paramagnetic shifts of **3** reflect simultaneous contributions of two spin density sources, i.e., the high-spin nickel(II) ion and a carbaporphyrin anion radical. For **3**, there are several electronic structures that need to be considered which are differentiated by the distributions of the unpaired electron spin densities and/or by the interactions between the magnetic centers. Thus, a metal-centered reduction results in the formation of a nickel(I) complex with a classical d^9 electronic configuration, e.g., PNi^{I}Ph (P = (2-NCH$_3$-21-CH$_3$CTPP)$^-$). On the other hand, a ligand-centered reduction produces a carbaporphyrin anion radical. The resulting electron configurations are as follows: (a) (P$^{\bullet-}$)Ni^{II}Ph antiferromagnetically coupled (Ni^{II}(h.s), $S = {}^1/_2$); (b) (P$^{\bullet-}$)Ni^{II}Ph ferromagnetically coupled ($S = {}^3/_2$); (c) (P$^{\bullet-}$)Ni^{II}Ph uncoupled or weakly coupled ($S = 1$, $S = {}^1/_2$).

In the case of [(2-NCH$_3$-21-CH$_3$CTPP)NiPh]$^-$, which is EPR silent in frozen toluene solution at 77 K, nickel-centered reduction can be excluded on the basis of the fact that nickel(I) in a macrocyclic environment is expected to display characteristic EPR spectra.[32,36,67−69] Typically, ^{1}H NMR spectra of d^9 metalloporphyrin ions are beyond detection, as T_{1e} is relatively long. Detectable NMR signals could be observed solely using deuterium NMR spectroscopy.[36,70] Similarly, porphyrin radicals typically reveal well-resolved EPR but not ^{1}H NMR spectra.[58,71] However once the interaction between two paramagnetic centers is accessible, the mutual interaction leads to the shortening of T_{1e}, affording well-resolved paramagnetic shifted ^{1}H NMR resonances, even for d^9 metal ions or anion porphyrin radicals.[49,58,60] Hence the ^{1}H NMR meso-phenyl resonance pattern of **3** is clearly consistent with the presence of the large π-spin density on the carbaporphyrin. This reflects the anion radical electronic structure of the equatorial ligand. Presumably the unpaired carbaporphyrin electron is localized in the π orbital having its spin density at the four selected pyrrole positions and two of the four meso-carbons. The remaining pyrrole shifts are due to the high-spin nickel(II) ion, as in **2**.

The origin of the direction of the meso-phenyl shifts in the ^{1}H NMR spectra of metal complexes containing porphyrin radicals has been a matter of interest. It appears that a correlation exists between these shifts and the coupling of porphyrin and metal spins.[52−57,62,64] For metalloporphyrin radicals in which the porphyrin and metal spins are antiferromagnetically coupled, the phenyl rings show downfield shifts for ortho and para protons and upfield shifts for meta protons. For complexes in which there is no antiferromagnetic coupling, the pattern is reversed; i.e., ortho and para resonances are located upfield and meta resonances downfield. Thus the meso-phenyl NMR features determined for **3** resemble the second situation, which excludes strong antiferromagnetic coupling in the ground electronic state.

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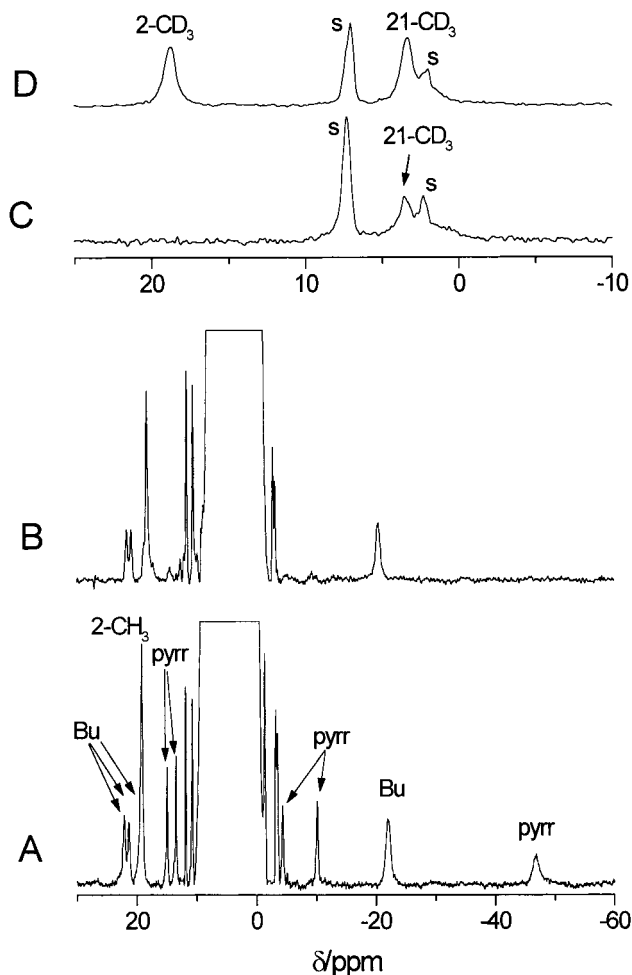(71) Fajer, J.; Davis, M. S. In *The Porphyrins*; Dolphin, D., Ed.; Academic Press: New York, 1979; p 198.

Figure 5. NMR spectra of **4**, formed by treating **1** with *n*-butyllithium in toluene at 203 K: (A) **1** = (2-NCH₃-21-CH₃CTPP)NiᴵᴵCl, C₇D₈, ¹H NMR; (B) **1** = (2-NCH₃-21-CH₃CTPP-*d₇*)NiᴵᴵCl, C₇D₈, ¹H NMR; (C) **1** = (2-NCH₃-21-CD₃CTPP)NiᴵᴵCl, C₇H₈, ²H NMR; (D) **1** = (2-NCD₃-21-CD₃CTPP)NiᴵᴵCl, C₇H₈, ²H NMR. Assignment of the dimethylated inverted porphyrin resonances is as in Figures 1 and 4; Bu = resonances of the coordinated σ-butyl ligand.

Reactions with Butyllithium. ¹H NMR titration of **1** (toluene-*d₈*) with *n*-butyllithium carried out at 203 K resulted in a spectroscopic pattern different from that determined in the analogous experiments using PhLi and PhMgBr (Figure 5). The novel species **4** does not decompose if kept in solution at 203 K. However, decomposition is observed when the temperature reaches 253 K. Under these experimental conditions, the process goes to completion in 0.5 h. Species **4** has also been detected using di-*n*-butylmagnesium as a carbanion source.

All resonances of **4** are located in the +30 to −50 ppm region (203 K). The species reveals six pyrrole resonances: two of them are shifted downfield (14.95, 14.38 ppm), but four of them, remarkably upfield (−3.45, −4.37, −10.16, −46.87 ppm (at 203 K)). We could not locate the seventh pyrrole resonance. With regard to the molecular structure, the observation of the paramagnetic shifted σ-butyl resonances (22.07, 21.36, 18.5, −21.91 ppm (at 203 K)) is of particular importance (Figure 5). It is consistent with the presence of a five-coordinate nickel ion coordinated to a σ-butyl ligand. The resonance of the 21-CH₃ (21-CD₃) group has been detected in the ²H NMR spectrum of [(2-NCH₃-21-CD₃CTPP)NiBu]ⁿ⁻ at 3.32 ppm (Figure 5, trace C). Its position is remarkable when compared to the cases of **1**−**3**, where large downfield shifts in the range 110−260 ppm have been observed. The 2-NCH₃ resonance has been unam-
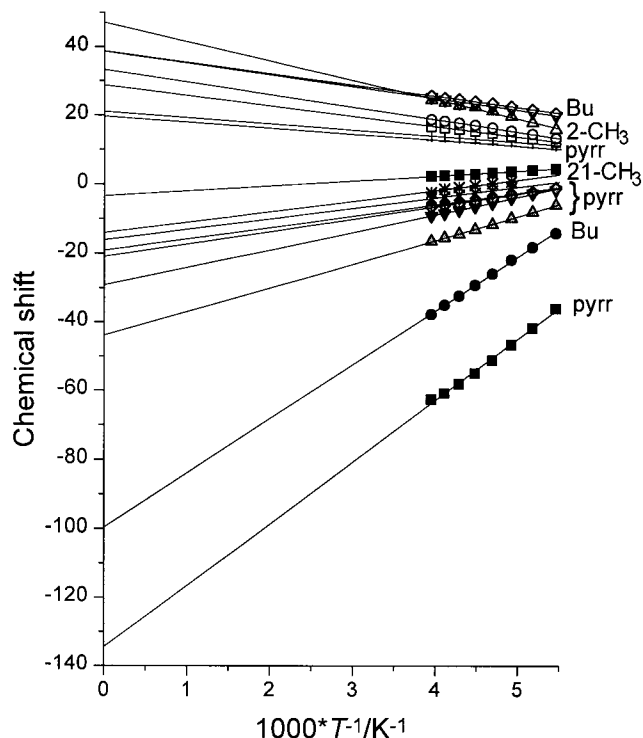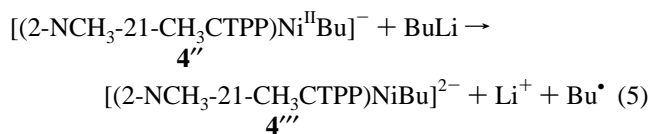
biguously identified at 19.17 ppm, since it is present in the spectrum of [(2-NCD₃-21-CD₃CTPP)NiBu]ⁿ⁻ (Figure 5, trace D). The remaining, paramagnetic shifted resonances shown in Figure 5 are assigned to meso-phenyl groups.

The Curie plots of the temperature dependence of the chemical shifts demonstrate pronounced anti-Curie behavior (Figure 6), which is unique for the whole collection of nickel(II) heteroporphyrins and nickel(II) carbaporphyrins,³¹⁻³⁹ including the new organometallic derivatives **2** and **3** described above. Qualitatively, the temperature dependence of the hyperfine shifts of **4** can be interpreted in terms of a temperature-dependent spin equilibrium between diamagnetic and paramagnetic states with diamagnetic properties approached as the temperature is lowered.

Unlike the case of the (2-NCH₃-21-CH₃CTPP)NiᴵᴵCl−PhLi system, there is no direct NMR evidence for the formation of several organometallic intermediates in the course of the titration of (2-NCH₃-21-CH₃CTPP)NiᴵᴵCl with *n*-butyllithium at 203 K. The new species could be a product of the replacement of the chloride ligand by the *n*-butyl anion to form (2-NCH₃-21-CH₃CTPP)NiᴵᴵBu (**4′**), i.e., the *n*-butyl analogue of **2**. Alternatively, the ligand exchange process could be accompanied by one-electron reduction by BuLi to generate the *n*-butyl analogue of **3**, i.e., [(2-NCH₃-21-CH₃CTPP)NiBu]⁻ (**4″**). Taking into account the reducing properties of *n*-butyllithium, the following reaction has been also considered:

$$[(2\text{-NCH}_3\text{-21-CH}_3\text{CTPP})\text{Ni}^{II}\text{Bu}]^- + \text{BuLi} \rightarrow$$
$$\mathbf{4''}$$
$$[(2\text{-NCH}_3\text{-21-CH}_3\text{CTPP})\text{NiBu}]^{2-} + \text{Li}^+ + \text{Bu}^\bullet \quad (5)$$
$$\mathbf{4'''}$$

The three hypothetical forms **4′**, **4″**, and **4‴** occur at three levels of oxidation, and in principle, they can be interconverted by one-electron-redox reactions by analogy to one-electron reduction of **2** to **3** using (TBA)BH₄. Consequently an attempt

was made to detect one of the missing forms of **4** by considering alternative pathways: $4'' \rightarrow 4'$; $4' \rightarrow 4''$; $4''' \rightarrow 4''$. However, oxidation of **4** with I_2 or reduction of **4** with (TBA)BH$_4$ failed to generate well-resolved paramagnetic shifted ^{1}H NMR spectra, which could be ascribed to the presence of another species analogous to [(2-NCH$_3$-21-CH$_3$CTPP)Ni^{II}Ph]$^{n-}$. Taking into account the fact that butyllithium is considered to be a stronger reducing reagent than phenyllithium, we suggest that, under these reaction conditions, [(2-NCH$_3$-21-CH$_3$CTPP)NiBu]$^-$ or the two-electron-reduced species [(2-NCH$_3$-21-CH$_3$CTPP)NiBu]$^{2-}$ can be trapped. A detailed comparison of the NMR spectra of **3** and **4** reveals a meaningful similarity in the patterns of the pyrrole resonances, at least at 263 K. However, the meso-phenyl groups of **4** show noticeably smaller shifts in comparison to those of **3**, and a striking difference is observed in the positions of the 21-CH$_3$ resonances. In light of the noticeable distinction in the extents of the paramagnetic shifts of **3** and **4** and the remarkable differences in the temperature dependences of the hyperfine shifts, we favor the formation of the two-electron-reduced species [(2-NCH$_3$-21-CH$_3$CTPP)NiBu]$^{2-}$.

The thermal equilibrium between two electronic states accessible for this overall oxidation state

$$(P^{\bullet-})Ni^I(ad_{z^2} + bd_{x^2-y^2})(S = 0) \rightleftharpoons$$
$$(P^{\bullet-})Ni^I(ad_{z^2} + bd_{x^2-y^2})(S = 1)$$
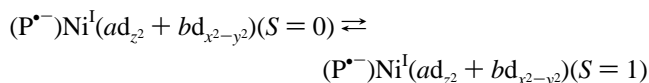
is consistent with the reverse temperature dependence of the paramagnetic shift vs $1/T$. The hyperfine shifts of **4** are related to the $(P^{\bullet-})Ni^IBu(S = 1)$ electronic state. On the basis of our previous conclusion, it is reasonable to expect that the overall downfield shifts of the pyrrole resonances are associated with delocalization through a σ-type molecular orbital. This implies the population of $(ad_{z^2} + bd_{x^2-y^2})$ by an unpaired electron and a downfield shift due to a σ-mechanism. However, the hypothetical contribution $(P^{\bullet-})Ni^I(d_{z^2})(S = 1)$, if dominating $(a^2 \rightarrow 1)$, would decrease the spin density on the macrocycle due to the nickel(I) ion, because the crucial for the transfer $d_{x^2-y^2}$ orbital is fully occupied. The very small paramagnetic shift of 21-CH$_3$ is directly accounted for by this model insofar as the downfield shift of this particular resonance can be considered a measure of the unpaired electron spin delocalization from the $d_{x^2-y^2}$ orbital. In the second extreme, the carbaporphyrin anion radical structure has to be considered analogous to that of **3**. This contribution, although smaller than for **3**, accounts for the upfield shifts of four pyrrole protons.

Decomposition. The observation of the solution behaviors of **2**−**4** revealed that these complexes were thermally stable at 203 K. At higher temperatures, their stabilities varied. While the NMR spectrum of **2** can be observed even at room temperature for about 20 min, warming of **3** resulted in its complete decomposition at 263 K after 30 min. In the case of **4**, decay of the NMR spectrum was observed over 15 min at 253 K. The decomposition process of **2** or **3** seems to be rather complex. The process yielded the two new compounds **5** and **6**, detected by EPR spectroscopy, which belong to the small class of organonickel(I) compounds.[33] Their relative concentrations varied in different experiments. Representative EPR spectra of **5** and **6** in frozen toluene solutions at 77 K are shown in Figure 7. The spectrum of species **5** (Figure 7, trace A) reveals the anisotropy of the **g** tensor $g_1 = 2.237$, $g_2 = 2.092$, $g_3 = 2.090$ and hyperfine coupling to three pyrrolic nitrogens ($A_{\parallel}^N = 9$ G, $A_{\perp}^N = 10$ G). The second product, **6** (Figure 7, trace B) is characterized by markedly different effective g values ($g_1 = 2.115$, $g_2 = 2.030$, $g_3 = 1.940$). The g_3 value, which is
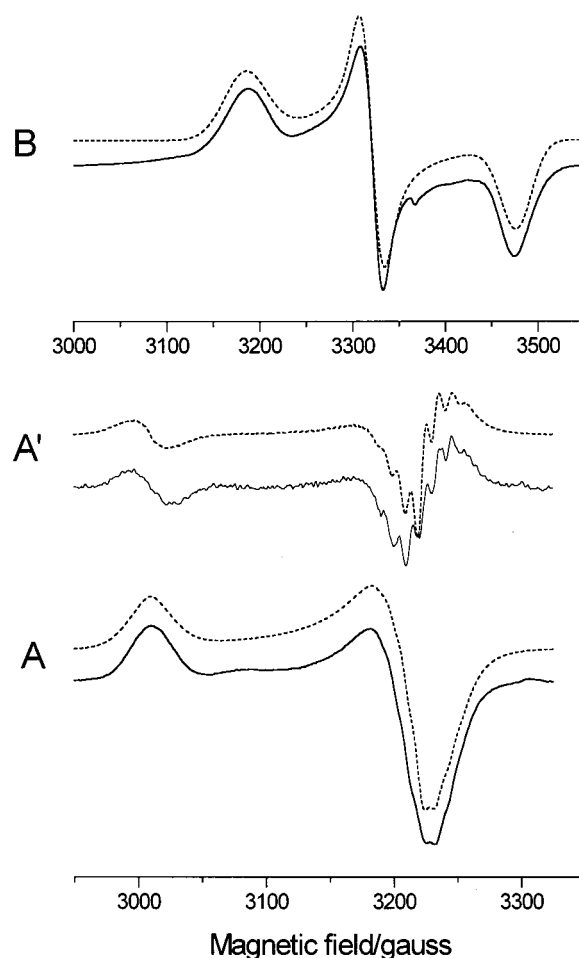

Figure 7. EPR results (toluene, 77 K): (A) spectra of **5**; (A′) second derivatives of spectra A showing hyperfine structure due to three ^{14}N nuclei; (B) spectra of **6**. The solid lines correspond to experimental spectra, and the simulated spectra are shown as dashed lines.

smaller than g_e, is particularly characteristic. Compound **6** could be prepared by independent synthetic routes, generating the same EPR spectrum. Reduction of **1** with zinc amalgam and the reaction of **1** with butyllithium or *sec*-butyllithium gave the same form **6** (vide infra). Thus, we conclude that **6** does not contain an apically bound aryl or alkyl ligand and is most likely four-coordinate. Importantly, a spectrum resembling that of **5** but with slightly different values for the **g** tensor components ($g_{\parallel} = 2.253$, $g_{\perp} = 2.106$) was detected in the course of the decomposition of [(2-NCH$_3$-21-CH$_3$CTPP)NiBu]$^{n-}$ (**4**).

One-electron reduction of nickel(II) porphyrinoids can result in three different limiting electronic structures, i.e., a nickel(I) macrocycle, a low-spin nickel(II) π-macrocyclic anion radical, and high-spin nickel(II) anion radical (see **3**). The description of the electron distribution in low-valent nickel porphyrins requires a molecular orbital which allows substantial spin density to be localized simultaneously on the nickel ion and the macrocycle. It is generally accepted that larger values of the **g** tensor and $g_i > g_e$ reflect a dominant contribution of the nickel(I) electronic structure. On the other hand, the g_i components approach g_e as the extent of localization of the electron density on the macrocycle increases.[36,38,39,67−69,72−80] Some one-electron-

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reduced nickel(II) chlorins and nickel(II) porphyrins yield a $g = 2$ signal, but the spectra are anisotropic with high-field shoulders at $g = 1.99$, accounted for by metal character added to the π-anion radicals.[69,75] Therefore, a low-spin nickel(II) porphyrin anion radical with some nickel(I) character gives spectra with $g_1 > g_2 > g_3$ and $g_3 < g_e$.[75] According to these criteria, the EPR spectrum of **5** reveals the Ni^I carbaporphyrin rather than the low-spin Ni^{II} anion radical electronic structure. On the other hand, the electronic structure of **6** can be considered as a low-spin nickel(II) carbaporphyrin anion radical with essential nickel(I) character. The spectral parameters of **6** are consistent with a report in the literature for one-electron-reduced nickel(II) *meso*-tetrakis(*o,o,m,m*-tetrafluoro-*p*-(dimethylamino)phenyl)porphyrin where similar **g** tensor values were noted.[75] Alternatively, we can rationalize the spectrum of **6** by two-electron reduction below $[(2\text{-}NCH_3\text{-}21\text{-}CH_3CTPP)Ni^{II}]^+$ to form $(2\text{-}NCH_3\text{-}21\text{-}CH_3CTPP)Ni$. The species can be considered as the biradical $(P^{\bullet-})Ni^I$ with $S = 1$. Such a description allows the satisfactory simulation of the experimental EPR spectrum using the parameters $g_{\parallel} = 2.025$, $g_{\perp} = 2.016$, $D = 144 \times 10^{-4}$ cm^{-1}, and $E = 48 \times 10^{-4}$ cm^{-1} in the SimFonia program. However, a half-resonant-field transition typical for a triplet state has not been observed in the experimental spectra.[81]

Characterization of the compositions of **5** and **6** is less complete than that for the precursors **2** and **3** investigated by NMR spectroscopy. Initially, the thermally unstable, paramagnetic organonickel(II) complexes **2** and **3** can decompose via one-electron internal reductions or by dissociations of the anionic aryl ligands to produce the EPR-active $[(2\text{-}NCH_3\text{-}21\text{-}CH_3CTPP)\text{-}Ni]$ and $[(2\text{-}NCH_3\text{-}21\text{-}CH_3CTPP)Ni]^-$ species. We have previously suggested the anion radical electronic structure for the five-coordinate complex **3**, which gave well-resolved NMR spectra and was EPR silent. However, modification of the carbaporphyrinoid macrocycle via a reaction with phenyllithium or butyllithium as found for regular metalloporphyrins[82] or with generated radicals cannot be excluded as well. This aspect is currently under further investigation.

Conclusion

Porphyrin core modification has been demonstrated to be crucial in the relative stabilization of the unprecedented organometallic compounds of nickel(III), nickel(II), and nickel(I).[24,31–33] Here we have shown novel examples of paramagnetic organometallic nickel derivatives. Thus, the dimethylated inverted porphyrin $2\text{-}NCH_3\text{-}21\text{-}CH_3CTPPH$ stabilizes the organonickel complex $(2\text{-}NCH_3\text{-}21\text{-}CH_3CTPP)Ni^{II}Ph$, where the nickel−carbon fragment is efficiently protected in the macrocyclic environment but, in addition, the axial position is occupied by the σ-phenyl ligand. This is the quite uncommon case—apart from the previously reported $(O_2TPP)Ni^{II}Ph_2$—where two σ-carbon atoms are directly involved in coordination to the paramagnetic nickel(II) ion.[33] In the course of our investigation, we have trapped reduction products of $(2\text{-}NCH_3\text{-}21\text{-}CH_3CTPP)Ni^{II}Cl$ and $(2\text{-}NCH_3\text{-}21\text{-}CH_3CTPP)Ni^{II}Ph$. Of particular importance is the fact that the $[(2\text{-}NCH_3\text{-}21\text{-}CH_3CTPP)Ni^{II}Ph]^-$ form preserves the coordination to two carbon donors. This compound reveals a remarkable electronic structure simultaneously combining features of the high-spin nickel(II) σ-organometallic species and the carbaporphyrin anion radical.

Experimental Section

Materials. 2,21-Dimethyl-5,10,15,20-tetraphenyl-2-aza-21-carbaporphyrin ($2\text{-}NCH_3\text{-}21\text{-}CH_3CTPPH$), its deuterated derivatives $2\text{-}NCD_3\text{-}21\text{-}CD_3CTPPH$, $2\text{-}NCH_3\text{-}21\text{-}CD_3CTPPH$, $2\text{-}NCH_3\text{-}21\text{-}CH_3CTPPH\text{-}d_7$ deuterated at the pyrrole positions, and $2\text{-}NCH_3\text{-}21\text{-}CH_3CTPPH\text{-}d_{20}$ deuterated at the meso-phenyl positions, and their nickel(II) complexes were synthesized as described previously.[24]

The Grignard reagents (C_6H_5MgBr, C_6D_5MgBr), phenyllithium, *n*-butyllithium, *sec*-butyllithium, lithium triethylborohydride (Super-Hydride), and tetrabutylammonium borohydride were purchased from Aldrich.

Instrumentation. ^1H NMR (300 MHz) and ^2H NMR (46 MHz) spectra were recorded on a Bruker AMX 300 spectrometer operating in a quadrature detection mode. Usually 1000−10 000 scans were accumulated over a 15-kHz bandwidth with 16K data points and with a delay time of 100 ms. The signal-to-noise ratio was improved by apodization of the free induction decay, which typically induced 25-Hz broadening. The peaks were referenced against solvent resonances.

EPR spectra were obtained with a Bruker ESP 300E spectrometer. The magnetic field was calibrated with a proton magnetometer and EPR standards. The EPR spectra were simulated by assuming orthorhombic symmetry. The details of the EPR simulation for $S = \frac{1}{2}$ have been given elsewhere.[36,68] The simulation for the triplet ground state was carried out using the SimFonia program supplied by Bruker.

Electrochemical measurements were performed in THF with tetrabutylammonium perchlorate as the supporting electrolyte. Cyclic voltammograms were recorded for a potential scan rate ranging from 0.02 to 0.5 V/s using an EA9C apparatus (MIM, Kraków, Poland). A Pt-disk working electrode, a Pt-wire auxiliary electrode, and an Ag/AgCl reference electrode were employed.

Sample Preparation. Typically, a 3-mg sample of $(2\text{-}NCH_3\text{-}21\text{-}CH_3CTPP)Ni^{II}Cl$ (**1**) was dissolved in 0.5 cm^3 of oxygen-free toluene-d_8 directly in an NMR tube capped with a rubber septum cap. The sample was cooled to 193 K in an acetone slush bath, and the respective arylating (alkylating) reagent (the Grignard reagent, phenyllithium, butyllithium, or *sec*-butyllithium) was titrated into the NMR tube using a microsyringe. The sample was shaken vigorously and then immediately transferred to the NMR spectrometer which was maintained at 203 K. Samples of the reduced $(2\text{-}NCH_3\text{-}21\text{-}CH_3CTPP)Ni$ complex for EPR measurements were prepared by stirring **1** with a suspension of fine-powdered zinc amalgam for 2 h under inert atmosphere. The reductant was then removed by filtration, and the filtrate was used as a stock solution.

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