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Paramagnetic σ-Bonded Phenylnickel(II) Macrocyclic Systems. Nuclear Magnetic Resonance Identification of (σ-Phenyl)nickel(II) 5,20-Diphenyl-10,15-bis(*p*-tolyl)-21-thiaporphyrin and (σ-Phenyl)nickel(II) *N*-Methyltetraphenylporphyrin[†]

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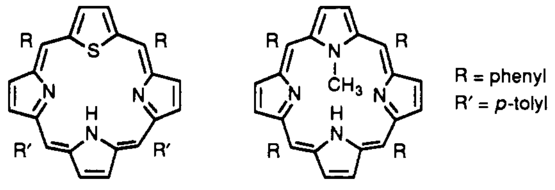
Addition of the phenyl Grignard reagent to toluene or dichloromethane solutions of nickel(II) monohalide complexes of 5,20-diphenyl-10,15-bis(*p*-tolyl)-21-thiaporphyrin (SDPDTPH) and *N*-methyltetraphenylporphyrin (NCH$_3$TPPH) at –70 °C resulted in formation of paramagnetic (σ-phenyl)nickel(II) derivatives which were characterized by means of ^{1}H NMR and ^{2}H NMR. The coordination of the phenyl ligand has been proven by the unique downfield pattern of three phenyl resonances in the respective ^{2}H NMR spectra of (SDPDTP)Ni^{II}(C$_6$D$_5$) (**1**) and (NCH$_3$TPP)Ni^{II}(C$_6$D$_5$) (**2**) (**1**, ortho 616, meta 170.0, para 76.0; **2**, ortho 568, metal 148.0, para 62.8; –70 °C, in ppm vs TMS in toluene). The (σ-phenyl)nickel(II) derivatives are in the high-spin paramagnetic electronic state: $d_{xy}^2 d_{xz}^2 d_{yz}^2 d_{z^2}^1 d_{x^2-y^2}^1$. The protons of the nickel-bound phenyl group display substantial hyperfine shifts which are dominated by the σ-contact contribution. A contact shift pattern established for phenyl ligand resembles that of pyridine in a large variety of nickel(II) pyridine complexes as both ligands are isoelectronic. A homolytic cleavage of the Ni^{II}–C bond has been observed for (SDPDTP)Ni^{II}(C$_6$H$_5$) in toluene with formation of (SDPDTP)Ni^I. The decomposition of (NCH$_3$TPP)Ni^{II}(C$_6$H$_5$) in toluene results in formation of (TPP)Ni^{II}, due to the demethylation.

Introduction

Organometallic chemistry of nickel(II) is of current interest in connection with the mechanisms of reactions of metalloenzymes which contain nickel ion, i.e. methyl-S-coenzyme-M reductase and carbon monoxide dehydrogenase. Nickel(II) intermediate complexes bearing an axial methyl ligand have been included as crucial intermediates in both enzymatic cycles.[1,2] The numerous examples of diamagnetic alkyl (aryl) derivatives accompanied by phosphines, arsines, or cyclopentadienyl are well characterized.[3] Holm et al. presented suitable diamagnetic organonickel models of carbon monoxide dehydrogenase.[4] We have decided to probe the organonickel chemistry of selected nickel macrocycles related to porphyrins.

This approach should be relevant in exploring properties of factor F430, a nickel(II) tetrapyrrole whose structure corresponds to that of hydrocorphin (a highly saturated porphyrin).[5] In general, organonickel(II) compounds are diamagnetic, including rare derivatives of nickel(II) porphyrins.[6,7] Paramagnetic organonickel(II) compounds are extremely rare and for a very long period of time have been exemplified only by (σ-methyl)nickel(II) [(*R*,*R*,*S*,*S*)-*N*,*N*′,*N*″,*N*‴-tetramethylcyclam.[8] Recently, a paramagnetic σ-methyl derivative of F430 was prepared by in situ methylation.[9] So far formation of a paramagnetic arylnickel(II) compound has yet to be achieved.

In this project we have focused on arylnickel(II) complexes of two porphyrin-related ligands, i.e. *N*-methyltetraphenylporphyrin and 5,20-diphenyl-10,15-bis(*p*-tolyl)-21-thiaporphyrin:



SDPDTPH NCH$_3$TPPH

The nickel(II) complexes of these ligands share a basic five-coordinate structure with approximately square pyramidal geometry and an apical chloride.[10,11]

Results and Discussion

The reaction of metal halides with Grignard reagents is a classical synthetic route to generate σ-bonded alkyl (aryl) organometallic complexes including metalloporphyrins.[12,13] Potentially the axial chloride of (SDPDTP)Ni^{II}Cl or (NCH$_3$TPP)Ni^{II}Cl can be replaced by aryl from the respective Grignard reagent. The detailed ^{1}H NMR characterizations of (NCH$_3$TPP)Ni^{II}Cl and (STPP)Ni^{II}Cl[10,14] have been completed. This technique has been applied as a suitable tool to follow the generation of (σ-phenyl)nickel(II) derivatives in reaction mixtures at low temperature in anaerobic conditions. It has generally been assumed that high-spin aryl complexes would be rather unstable.[3,4,8]

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[†] Abbreviations: STPP, 5,10,15,20-tetraphenyl-21-thiaporphyrin anion; STPP-*d*$_{10}$, 5,20-diphenyl-10,15-bis(phenyl-*d*$_5$)-21-thiaporphyrin anion; STPP-*d*$_6$, 5,10,15,20-tetraphenyl-21-thiaporphyrin anion deuterated at pyrrole β-positions; SDPDTP, 5,20-diphenyl-10,15-bis(*p*-tolyl)-21-thiaporphyrin anion; NCH$_3$TPP, *N*-methyltetraphenylporphyrin anion; NCH$_3$TPPH-*d*$_8$, *N*-methyltetraphenylporphyrin anion deuterated at pyrrole β-positions.

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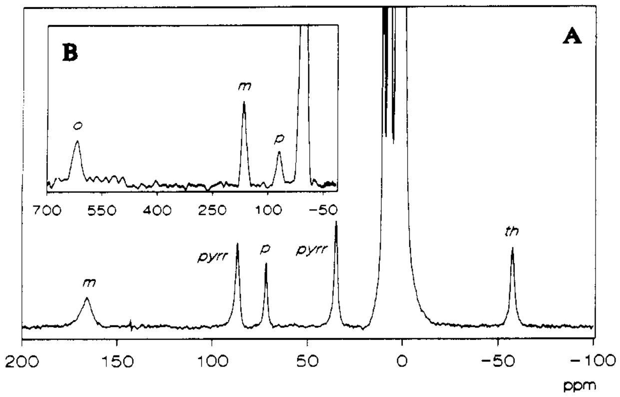

Figure 1. NMR spectra of (σ-phenyl)nickel(II) 21-thiaporphyrin complexes: (A) (SDPDTP)Ni^{II}(C$_6$H$_5$) (300-MHz ^{1}H NMR); (B) (SDPDTP)Ni^{II}(C$_6$D$_5$) (46.06-MHz ^{2}H NMR). Spectra are taken in toluene solutions (A, C$_7$D$_8$; B, C$_7$H$_8$) at −70 °C. Assignments of resonances: pyrr, pyrrole; th, thiophene; *o*, ortho phenyl, *m*, meta phenyl, and *p*, para phenyl, protons (deuterons) of σ-bonded phenyl ligand.

Addition of phenyl Grignard reagents (ArMgBr, where Ar = C$_6$H$_5$, C$_6$D$_5$, *p*-CH$_3$C$_6$H$_4$, *m*-CH$_3$C$_6$H$_4$, and *o*-CH$_3$C$_6$H$_4$ in THF or diethyl ether) to toluene or dichloromethane solutions of (NCH$_3$TPP)Ni^{II}Cl or (SDPDTP)Ni^{II}Cl at −70 °C resulted in formation of the respective phenyl derivatives according to the reactions

$$\text{(SDPDTP)Ni}^{\text{II}}\text{Cl} + \text{ArMgBr} \rightarrow \text{(SDPDTP)Ni}^{\text{II}}\text{Ar} + \text{MgBrCl}$$

$$\text{(NCH}_3\text{TPP)Ni}^{\text{II}}\text{Cl} + \text{ArMgBr} \rightarrow \text{(NCH}_3\text{STPP)Ni}^{\text{II}}\text{Ar} + \text{MgBrCl}$$

as followed in the reaction mixtures by NMR spectroscopy. The corresponding ^{1}H NMR and ^{2}H NMR spectra of (SDPDTP)-Ni^{II}Ar are presented at Figures 1–3. The relevant data for (NCH$_3$STPP)Ni^{II}Ar are shown at Figure 4.

The resonance assignments have been based on the intensity data, line width analysis, and methyl-substitution effects (Figure 2) as well as on the selective deuteration. The following selectively deuterated porphyrins have been used: STPPH-*d*$_{10}$, STPPH-*d*$_6$, and NCH$_3$TPPH-*d*$_8$.

The coordination of the phenyl ligand is clearly demonstrated by the unique downfield pattern of three phenyl resonances in the respective ^{2}H NMR spectra of (SDPDTP)Ni^{II}(C$_6$D$_5$) (Figure 1, trace B) and (NCH$_3$TPP)Ni^{II}(C$_6$D$_5$) (Figure 4, trace B) and their deuterated analogs (STPP-*d*$_6$)Ni^{II}(C$_6$D$_5$), (STPP-*d*$_{10}$)-Ni^{II}(C$_6$D$_5$), and (NCH$_3$TPP-*d*$_8$)Ni^{II}(C$_6$D$_5$). Two of the phenyl resonances are also identified in the ^{1}H NMR spectra of (SDPDTP)Ni^{II}(C$_6$H$_5$) (Figure 1, trace A) and (NCH$_3$TPP)-Ni^{II}(C$_6$H$_5$) (Figure 4, traces A and C) once they have been identified previously by ^{2}H NMR. Integration of the axial *para*-phenyl and pyrrole resonances, which are located in a similar spectral range and have similar line widths, indicated 1:1 σ-bonded phenyl ligand to nickel(II) stoichiometry. The characteristic paramagnetic shifts are collected in Table I together, for the sake of comparison, with the respective shifts of the maternal chloro complexes. The small σ-phenyl shift differences have been determined (−70 °C) in samples prepared by addition of the Grignard reagent dissolved in THF or ethyl ether. It suggests a rapid chemical exchange between (SDPDTP)Ni^{II}(C$_6$H$_5$) and (SDPDTP)Ni^{II}(C$_6$H$_5$)(THF), the second species being formed in small concentration. On the basis of the paramagnetic shift data, one can conclude that in both cases the (σ-phenyl)nickel(II) derivatives are in the high-spin paramagnetic electronic state $d_{xy}^2d_{xz}^2d_{yz}^2d_{z^2}^1d_{x^2-y^2}^1$. One of the unpaired electrons is located on the σ-molecular orbital, which consists of the Ni^{II} (d_{z^2}) and σ-phenyl orbitals. The large σ-contact shifts, as discussed below, provide experimental evidence for such a description of the electronic structure.

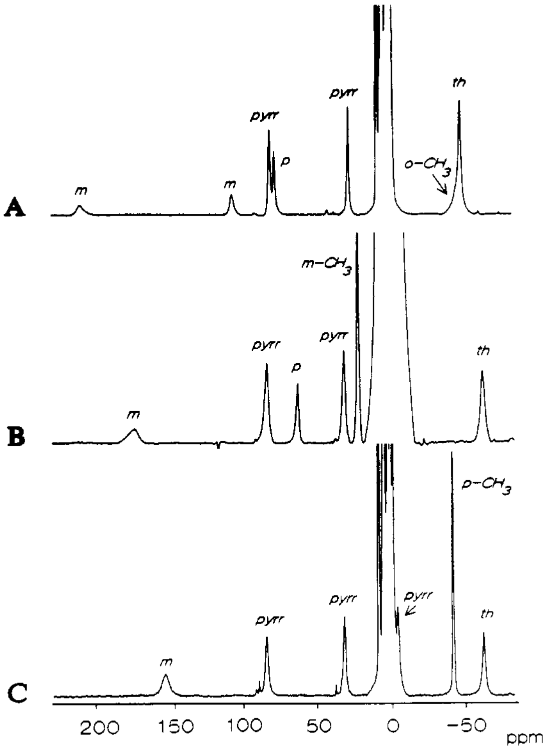

Figure 2. 300-MHz ^{1}H NMR spectra of (σ-tolyl)nickel(II) 21-thiaporphyrin complexes: (A) (SDPDTP)Ni^{II}(*o*-CH$_3$C$_6$H$_4$); (B) (SDPDTP)Ni^{II}(*m*-CH$_3$C$_6$H$_4$); (C) (SDPDTP)Ni^{II}(*p*-CH$_3$C$_6$H$_4$). All spectra are taken in toluene-*d*$_8$ solutions at −70 °C. Assignments of resonances: pyrr, pyrrole; th, thiophene; *o*, *m*, *p*, *p*-CH$_3$, *m*-CH$_3$, *o*-CH$_3$, proton or methyl resonances of σ-bonded tolyl ligands. The broad *o*-CH$_3$ and narrow thiophene resonances overlap at −45.4 ppm as established by integration and deconvolution.

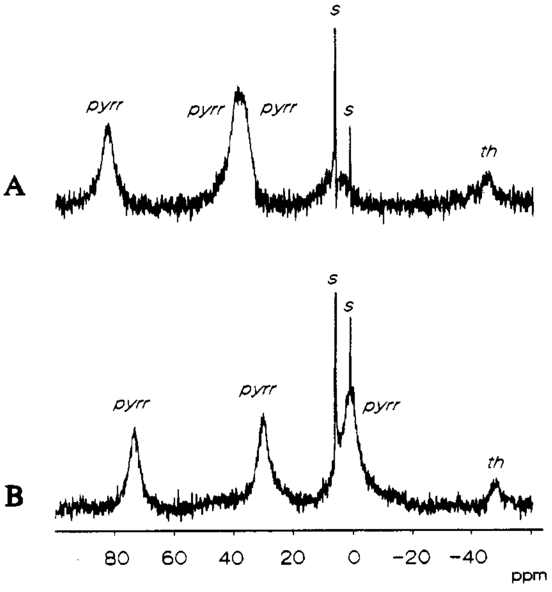

Figure 3. 46.06-MHz ^{2}H NMR spectra of nickel(II) 21-thiaporphyrin complexes: (A) (STPP-*d*$_6$)Ni^{II}Cl (B) (STPP-*d*$_6$)Ni^{II}(C$_6$H$_5$). The relatively small apodization of the free induction decay which induced 1-Hz broadening was used to achieve the satisfactory resolution in the crucial −5 ppm to 5 ppm region where one of pyrrole resonances is located. Both spectra are taken in toluene solutions at −40 °C in order to decrease line widths. Resonance assignments are as in Figures 1 and 2; s = solvent.

Patterns of NMR spectra determined for equatorial macrocycles of phenyl and chloro derivatives are similar. The observed

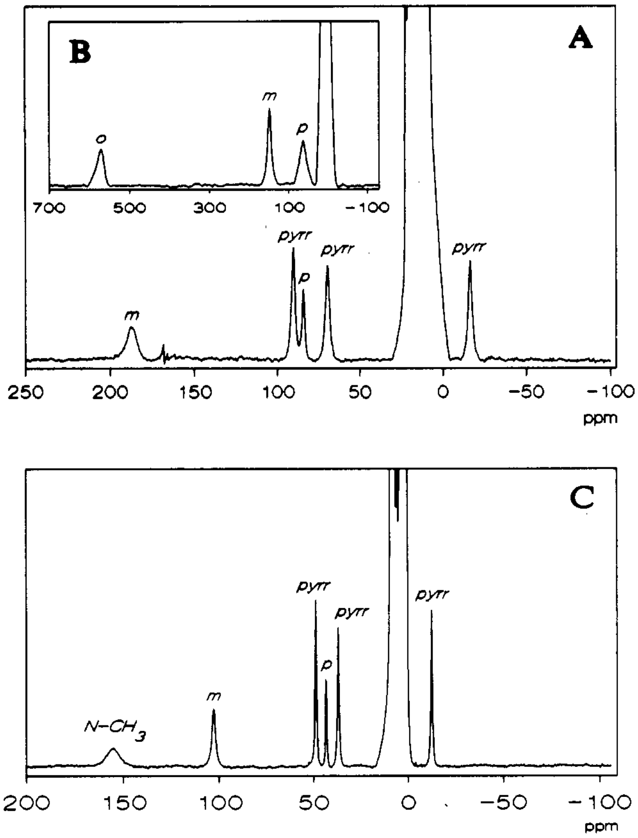

Figure 4. NMR spectra of (σ-phenyl)nickel(II) *N*-methylporphyrin complexes: (A) $(NCH_3TPP)Ni^{II}(C_6H_5)$ at -70 °C; (B) $(NCH_3TPP)Ni^{II}(C_6D_5)$ at -70 °C; (C) $(NCH_3TPP)Ni^{II}(C_6H_5)$ at 20 °C. Traces A and C are 300-MHz ^{1}H NMR spectra in toluene-d_8. Trace B is the ^{2}H NMR spectrum of selectively deuterated species in toluene. In the course of experiment C a gradual demethylation of $(NCH_3TPP)Ni^{II}(C_6H_5)$ was established. Resonance assignments: pyrr, pyrrole; *o*, *m*, *p*, ortho, meta, and para protons of σ-bonded phenyl ligand; N–CH$_3$, methyl resonance of the N-methylated pyrrole.

Table I. ^{1}H NMR and ^{2}H NMR Data for (σ-Phenyl)nickel(II) Complexes in Toluene at -70 °C

ligand	chem shifts in ppm vs TMS						
	σ-phenyl[a]			pyrrole			thiophene or N-methylated pyrrole
	ortho	meta	para				
			(SDPDTP)Ni^{II}				
Cl				97.6	46.4	41.7	-56.4
C_6H_5[d]	*e*	166.7	72.3	87.0	35.4	*g*	-58.0
C_6D_5[b,c]	616	170.0	76.0				
p-$CH_3C_6H_4$[c]	*e*	152.8	(-39.1)	87.0	33.9	-1.4	-58.8
m-$CH_3C_6H_4$[c]	*e*	174.0 (24.6)	66.0	87.0	35.0	*f*	-58.8
o-$CH_3C_6H_4$[c]	*e* (-44.3)	208.7 109.0	80.7	84.3	31.6	*f*	-45.4
			(NCH$_3$TPP)Ni^{II}				
Cl				75.7	70.1	30.3	-14.24
C_6D_5[b,c]	568	148.0	62.8				
C_6H_5[d,i]	*e*	157.7	66.0	72.6	52.0	*h*	-21.5

[a] In parentheses are shifts for corresponding methyl groups. [b] ^{2}H NMR spectra. [c] The Grignard reagent was added in THF solution. [d] The Grignard reagent was added in diethyl ether solution. [e] Not observed in the ^{1}H NMR spectrum due to the large contact shift and line width. [f] Covered by strong signals of THF or diethyl ether. [g] 2.0 ppm, observed only for (STPP-d_6)Ni^{II}(C_6H_5) at -40 °C (^{2}H NMR). [h] -0.7 ppm, observed only for (NCH$_3$TPP-d_8)Ni^{II}(C_6H_5) at 20 °C (^{2}H NMR). [i] N–CH$_3$, 154.7 ppm, observed only at 20 °C.

differences reflect only the impact of axial coordination. The change in the sign of the paramagnetic shift, established for only one of three pyrrole resonances of (STPP-d_6)Ni^{II}(C_6H_5) (Figure 3, trace B) as compared to (STPP-d_6)Ni^{II}Cl (Figure 3, trace A), can be accounted for by the competitive σ vs π delocalization mechanisms described in detail for the nickel(II) core-modified porphyrins.[10,14]

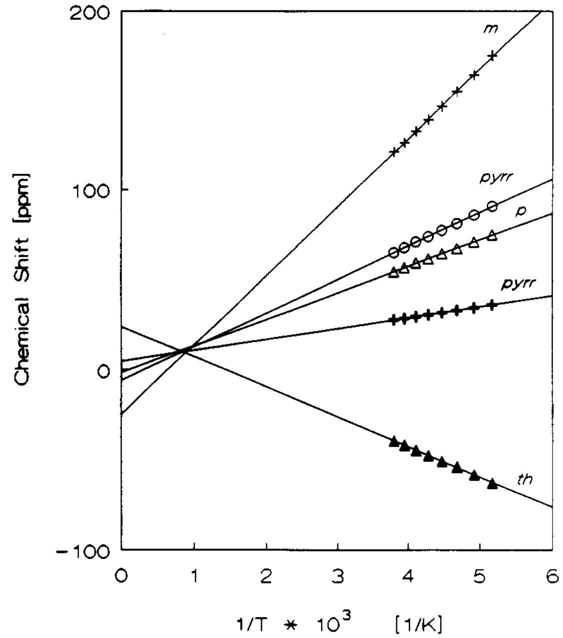

Figure 5. Plot of chemical shifts versus $1/T$ for (SDPDTP)Ni^{II}(C_6H_5) in toluene-d_8. Assignments of resonances follow those from Figure 1.

A similar sign alternation of the paramagnetic shift for one of the pyrrole resonances has been established for the (NCH$_3$TPP)-Ni^{II}Cl and (NCH$_3$TPP)Ni^{II}(C_6H_5) couple as well (Table I). The downfield paramagnetic shift results from the σ-contact mechanism. The direct σ–π spin density transfer, possible due to the characteristic side-on coordination of thiophene or N-methylated pyrrole, produces the upfield contribution to thiophene, N-methylated pyrrole, and pyrrole paramagnetic shifts. The large difference of the contact shifts of pyrrole resonances observed previously for (STPP)Ni^{II}Cl and (NCH$_3$TPP)Ni^{II}Cl even for protons located on the same pyrrole ring results from this mechanism of spin density delocalization.[14] (SDPDTP)Ni^{II}(C_6H_5) and (NCH$_3$TPP)Ni^{II}(C_6H_5) present the case where one of the pyrrole resonances exhibits a contact shift dominated by the upfield contribution of the π-mechanism which results in the net upfield shift. A similar situation was described previously for (NCH$_3$-TPP)Fe^{II}Cl, where two pyrroles were shifted downfield, one upfield, and the N-methylated pyrrole resonance upfield.[15] The dipolar contribution to σ-phenyl of (SDPDTP)Ni^{II}(C_6H_5) or (NCH$_3$TPP)Ni^{II}(C_6H_5), estimated as previously,[10,14] is relatively small.

Curie plots (Figure 5) of the temperature dependence of the chemical shifts of the thiophene, pyrrole, and *meta*- and *para*-phenyl resonances of (SDPDTP)Ni^{II}(C_6H_5) show linear behavior with extrapolated intercepts that do not correspond to those of diamagnetic references.[16] For a high-spin Ni^{II} ion the dipolar shift can arise mainly as a result of anisotropy of zero-field splitting.[10]

The Curie plot indicates some dipolar contributions at these positions as the ZFS related dipolar shift would produce the T^{-2}-dependent curvature.[10] However, the observed alternation of the direction of the *meso*-phenyl shift is compatible with a dominant contact contribution to the paramagnetic shift.[14] The contact shifts for the nickel-bound phenyl group clearly indicate

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(16) As diamagnetic core modified σ-phenyl-coordinated metallothiaporphyrins are not known, the shifts of diamagnetic chloride derivatives for pyrrole resonances and (TPP)In(C_6H_5) for phenyl shifts have been used.[17]

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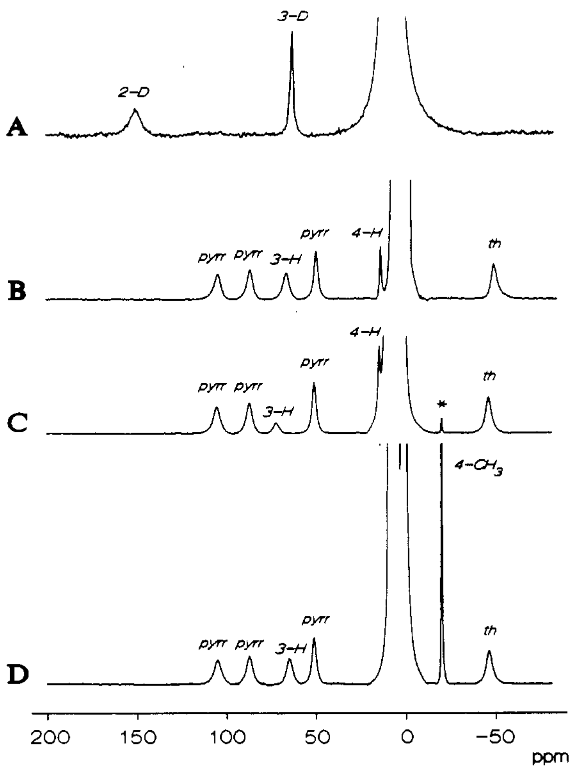

Figure 6. NMR spectra of nickel(II) 21-thiaporphyrin pyridine adducts: (A) $[(SDPDTP)Ni^{II}(C_5D_5N)_2]Cl$; (B) $[(SDPDTP)Ni^{II}(C_5H_5N)_2]Cl$; (C) $[(SDPDTP)Ni^{II}(3\text{-}CH_3C_5H_4N)_2]Cl$; (D) $[(SDPDTP)Ni^{II}(4\text{-}CH_3\text{-}C_5H_4N)_2]Cl$. All spectra are taken in dichloromethane solutions (CH_2Cl_2, CD_2Cl_2, respectively) at −70 °C. A total of 10 equiv of pyridine (picoline) ligand has been added. Trace A is the ^2H NMR spectrum of selectively deuterated species. Traces B–D are 300-MHz ^1H NMR spectra. Resonance assignments: pyrr, pyrrole; th, thiophene; 2-H (2-D), 3-H (3-D), 4-H (4-D), 3-CH_3, 4-CH_3 of pyridine or picoline ligands; asterisk in trace C denotes the 4-CH_3 resonance of 4-picoline, which is present as the impurity in 3-picoline.

the presence of a σ-delocalization mechanism. It attenuates in the order ortho > meta > para with increasing distance from nickel.

The methyl substitutions at the para and ortho positions result in the sign reversal of the contact shift as expected in the case of the σ–π polarization mechanism.[18] The shift pattern established for the phenyl ligand resembles that of pyridine (picoline) in $[(STPP)Ni^{II}(R\text{-}C_6H_4N)_2]Cl$, where R = H, 3-$CH_3$, and 4-$CH_3$ (Figure 6), and in a large variety of nickel(II) pyridine complexes as both ligands, i.e. $C_6H_5^-$ and C_6H_5N, are isoelectronic.[18]

We have shown previously that the pyrrole shift pattern of Ni(II) 21-thiaporphyrin complexes reflects the Ni(II) coordination number.[14] The characteristic pattern of the pyrrole resonances, established for the pyridine adduct, suggests formation of six-coordinated species. However, only one out of two pyridine ligands is seen in ^1H NMR spectrum as established by integration of the corresponding resonances. The second pyridine ligand remains in fast exchange with the uncoordinated pyridine. In the case of slow exchange two sets of the pyridine resonances should be observed. Both sides of $[(STPP)Ni^{II}(R\text{-}C_6H_4N)_2]Cl$ are not equivalent, as the thiophene moiety is bent out from the thiaporphyrin plane.[11,14] Such differentiation of the coordinated axial ligands was observed for 5-methylimidazole bis(adducts) of iron(III) *N*-methylporphyrins.[19]

The pyridine ligand shifts in $[(STPP)Ni^{II}(R\text{-}C_6H_4N)_2]Cl$ are as follows: 2-H 156.3, 3-H 68.4, 4-H 17.2 (−18.5) (in ppm vs TMS; −70 °C in CD_2Cl_2; in parentheses the shift of the methyl peak found for 4-picoline). Addition of 2-picoline produced the pyrrole pattern which is typical for a six-coordinate adduct, but under the conditions of our experiment we did not observe any resonances of the axial ligand.

The stronger bonding in the phenyl case produces relatively larger contact shifts. The σ-phenyl NMR pattern observed for (σ-phenyl)nickel complexes seems to be the first example where the phenyl ligand shift is dominated by the σ-contact contribution. Analysis of the contact shift for low-spin iron(III) tetraarylporphyrins and iron(IV) tetraarylporphyrins bearing an axial aryl ligand indicated the large π-spin density in the axial ligand as the contact shift decrease in the characteristic order ortho > para > meta.[20] The corresponding high-spin derivatives require fluorinated aryl ligands that preclude direct comparison.[21] In analogy to alkyl complexes of low-spin iron(III) porphyrins[22] some contribution of the σ-contact mechanism to the generally accepted π-mechanism[20,21] should be postulated for phenyliron(III) porphyrins. An NMR pattern similar to that for phenylnickel(II) (ortho > meta > para) but in the upfield direction can be expected. Opposite signs for the σ-spin density transfer have been predicted for d^8 and low-spin d^5 complexes.[23] As a matter of fact, similar σ-delocalization patterns but in opposite directions were established in the two saturated, geometrically related ligands, i.e. for azaadamantane coordinated to nickel(II) and the adamantyl ligand coordinated to low-spin iron(III) porphyrin.[22,24]

The σ-phenyl-ligated nickel(II) complexes are stable in −70 °C in toluene. As temperature is increased, we have observed their gradual decomposition under the conditions of our experiments. The homolytic cleavage of the Ni^{II}–C bond has been observed for $(SDPDTP)Ni^{II}(C_6H_5)$ in toluene and dichloromethane with formation of $Ni^I(SDPDTP)$ as determined by characteristic ESR ($g_1 = 2.109$; $g_2 = 2.040$; $g = 2.030$)[25] and NMR spectra. On warming to −50 °C an ionic dissociation of σ-bound phenyl has been also found in dichloromethane. The decomposition of $(NCH_3TPP)Ni^{II}(C_6H_5)$ in toluene results in formation of $(TPP)Ni^{II}$, established by characteristic electronic and NMR spectra, due to a demethylation process which is typical for N-methylated metalloporphyrins.[10]

The spectrum of $(NCH_3TPP)Ni(C_6H_5)$ has been taken also at 20 °C (Figure 4, trace C) directly after the generation of the σ-phenyl species. Almost complete decomposition to $(TPP)Ni^{II}$ was established after the data acquisition (500 scans). We would like to point out that $(NCH_3TPP)Ni^{II}(C_6H_5)$ belongs to a rather not numerous class of organometallic forms of N-alkylated metalloporphyrins.[26,27] Attempts are under way to investigate reactivity aspects of these rare paramagnetic organonickel(II) compounds.

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Experimental Section

Materials. Tetraphenyl-21-thiaporphyrin and its methyl derivative SDPDTPH were synthesized as described recently.[25] STPPH-d_6 (deuterated at pyrrole β-positions) was prepared from pyrrole-d_5.[28,29] Partial deuteration of thiophene β-position in the course of this procedure was established. STPPH-d_{10} was synthesized in the same manner as STPPH using benzaldehyde-d_5.[14] NCH_3TPPH and NCH_3TPPH-d_8 were synthesized by a previously reported method.[10]

All nickel(II) 21-thiaporphyrins and *N*-methylporphyrins including selectively deuterated derivatives were synthesized as described for the nickel(II) insertion procedures.[10,11,14] Grignard reagents C_6H_5MgBr and C_6D_5MgBr were purchased from Aldrich. The *p*-$CH_3C_6H_4MgBr$, *m*-$CH_3C_6H_4MgBr$, and *o*-$CH_3C_6H_4MgBr$ derivatives were synthesized according to standard procedures from the respective bromoaryl derivatives.[30]

Pyridine, 2-picoline, 3-picoline, 4-picoline (all from Merck), and pyridine-d_5 (Aldrich) were used as received.

Sample Preparation. A sample of 5 mg of nickel(II) porphyrin was dissolved in 0.5 cm^3 of oxygen-free toluene directly in a NMR tube capped with a rubber septum cap. The sample was cooled to −80 °C in a bath of dry ice and acetone, and the Grignard reagent was titrated into the NMR tube via a syringe. The sample was shaken vigorously and then immediately transferred to an NMR spectrometer which was maintained at −70 °C.

Instrumentation. ^1H NMR and ^2H NMR spectra were measured on a Bruker AMX 300 spectrometer operating in a quadrature detection mode (^1H, 300 MHz; ^2H, 46.06 MHz). Usually 10 000 scans were accumulated with a delay time of 50 ms for each ^2H NMR spectrum. The ^2H NMR spectra were collected over 30 kHz or 7.5 kHz bandwidths with 4 K data points. The signal to noise ratio was improved by apodization of the free induction decay, which induced typically 25–50-Hz broadening. The peaks were referenced against solvent resonances. A total of 1000 scans were taken for the ^1H NMR spectra over a 15-kHz bandwidth with 16 K data points. The probe temperature was calibrated by Van Geet's method.[31] To separate overlapping resonances, the spectra were deconvoluted by using the deconvolution routine of the Bruker AMX 300 software. ESR spectra were obtained with a Radiopan SE/X spectrometer.

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