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Organonickel Complexes of 21,23-Dioxaporphyrin. Identification of the Paramagnetic Organonickel(II) Complex with Two η^1-Phenyl Ligands

Piotr J. Chmielewski and Lechosław Latos-Grażyński*

Department of Chemistry, University of Wrocław, 14 F. Joliot-Curie Street, 50-383 Wrocław, Poland

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Addition of aryl Grignard reagents [PhMgCl, PhMgBr, (Ph-d_5)MgBr, (*o*-MePh)MgBr, (*m*-MePh)MgBr] dissolved in ethyl ether or THF to toluene solutions of nickel(II) dihalide complexes of 5,10,15,20-tetraphenyl-21,23-dioxaporphyrin (O_2TPP), **1**, at 203 K resulted in formation of a variety of rare paramagnetic σ-organonickel(II) species that have been detected and subsequently characterized by ^{1}H and ^{2}H NMR. The stoichiometry and the spectral pattern of the formed complexes depend strongly on the counteranion present in the Grignard reagent. Titration of PhMgCl to **1**-Cl (203 K) led to the substitution of only one chloride ligand by the phenyl anion, yielding (O_2TPP)Ni^{II}(Ph)Cl (**2**). The coordination of a σ-phenyl ligand has been proven by the downfield pattern of two observed phenyl resonances at 243K (129.20 (*m*), 63.71 ppm (*p*)) accompanied by downfield furan (31.53 ppm) and pyrrole (25.85 ppm) resonances of equatorial O_2TPP. Titration with PhMgBr resulted in formation of the different monophenyl adduct (O_2TPP)Ni^{II}(Ph)Br (**3**) and the first paramagnetic organonickel(II) complex with two σ-aryl ligands, i.e., the bisphenyl adduct (O_2TPP)Ni^{II}(Ph)$_2$ (**4**). Both **3** and **4** have revealed the ^{1}H NMR upfield-shifted patterns with no parallel to any nickel(II) porphyrin or heteroporphyrin (**3**, −165.21 ppm (pyrr), −54.49 ppm (f); **4**, −143.05 ppm (pyrr), −31.35 ppm (f), 243 K). The ortho, meta, and para proton resonances of **3** are located in the typical low-field region (558 ppm (*o*), 153.46 ppm (*m*), 71.58 ppm (*p*) at 243 K). In contrast, the phenyl signals of **4** have been detected in the strikingly narrow region (8 to −10 ppm). An interpretation of this spin delocalization requires a change of the nickel(II) ion ground state from $(d_{xy})^2(d_{xz})^2(d_{yz})^2(d_{z^2})^1(d_{x^2-y^2})^1$ determined for **2** to $(d_{xy})^2(d_{x^2-y^2})^2(d_{yz})^2(d_{z^2})^1(d_{xz})^1$ and $(d_{xy})^2(d_{x^2-y^2})^2(d_{z^2})^2(d_{yz})^1(d_{xz})^1$ configurations for **3** and **4**, respectively. Warming of **2**, **3,** or **4** resulted in their decomposition to produce the σ-phenylnickel(I) 21,23-dioxaporphyrin (O_2TPP)Ni^I(Ph) **6** identified by EPR studies ($g_1 = 2.411$; $g_2 = 2.161$; $g_3 = 2.049$). This species has been also generated by an independent route reacting (O_2TPP)Ni^{I}Br with the Grignard reagent.

Introduction

Organometallic chemistry of nickel(II) attracts much attention due to an involvement of organonickel species in the mechanisms of reactions of metalloenzymes such as methyl-*S*-coenzyme-M reductase, carbon monoxide dehydrogenase (CODH), and acetyl coenzyme A synthase, found in certain methanogenic, acetogenic, and sulfate-reducing bacteria. The intermediate complex containing an apical methyl ligand coordinated to the Ni(II) ion has been proven to be a crucial intermediate in enzymatic cycle of CODH, and its existence has been proposed in the case of methyl coenzyme reductase and acetyl coenzyme A synthase.[1−4] In particular, factor 430 (F_{430}), a nickel(II) tetrapyrrole the structure of which corresponds to that of a hydrocorphin, was identified in the prosthetic group of methyl coenzyme-M reductase.[2,5−7] It contains divalent, pseudo-octahedral (d^8, $S = 1$) nickel ion, but a Ni(I) (d^9, $S = {}^1/_2$) oxidation state is a likely catalytic transient.

Although the numerous examples of diamagnetic alkyl or aryl derivatives accompanied by phosphines, arsines, and cyclopentadienyl are well characterized,[8] the paramagnetic organometallic nickel(II) complexes are rather exotic and typically unstable, though with some remarkable exceptions.[9−12] Our contribution to the field includes a σ-phenyl coordination to the nickel(II) ion located within the 21-heteroporphyrin environment.[13,14] The relevant nickel(II) complexes share a basic five-coordinate structure with an approximately square pyramidal geometry and an apical σ-phenyl. Despite thermal instability, their formation has been directly confirmed by means of ^{1}H and ^{2}H NMR. The determined hyperfine shift patterns presented several useful and

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* Corresponding author. E-mail llg@wchuwr.chem.uni.wroc.pl.

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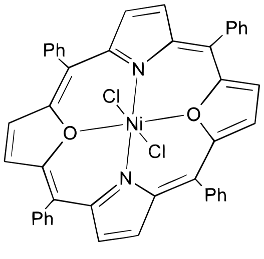
Table 1. NMR Data for Nickel(II) 21,23-Dioxaporphyrin Complexes[a]

ligands; abbreviation	pyrrole	furan	phenyl
$2Cl^-$; **1**-Cl[b]	64.11	41.8	–
$2Br^-$; **1**-Br	69.09	50.00	–
Ph^-, Cl^-; **2**	31.53	25.85	129.20 (*m*), 63.71 (*p*)
m-$MePh^-$, Cl^-; **2**-*m*-Me[b]	31.08	25.32	143.06 (*m*), 61.16 (*p*), 22.44 (*m*-CH_3)
Ph^-, Br^-; **3**	−165.21	−54.49	558 (*o*)[c], 153.46 (*m*)[c], 71.58 (*p*)[c]
o-$MePh^-$, Br^-; **3**-*o*-Me[d]	−202.2	−72.47	193.2 (m_1), 119.09 (m_2), 82.02 (*p*), −34.77 (*o*-CH_3)
$2Ph^-$; **4**	−143.05	−31.35	5.5 (*o*)[c], −4.47 (*m*)
2(*m*-$MePh^-$); **4**-*m*-Me	−146.07	−32.44	−6.51 (*m*)
$2CN^-$; **1**-CN[e]	36.55	26.70	–
$2PhO^-$; **1**-PhO[e]	51.11	38.14	16.67 (*m*), −17.45 (*o*), −20.28 (*p*)
2py; **1**-py[f]	54.78	17.81	–

[a] Spectra taken in toluene-d_8 at 243 K, unless stated otherwise. [b] 223 K. [c] ^{2}H NMR data of coordinated $C_6D_5^-$. [d] 215 K. [e] 293 K, $CDCl_3$. [f] 223 K, $CDCl_3$.

Chart 1



1-Cl

potentially unique probes (Table 1) for detecting (σ-phenyl)nickel(II) heteroporphyrin derivatives which are in the well-defined, high-spin ground electronic state $(d_{xy})^2(d_{xz})^2(d_{yz})^2(d_{z^2})^1(d_{x^2-y^2})^1$.

Recently[15] we reported the synthesis and the structure of the first metal complex of a neutral, porphyrin-related macrocycle, namely, nickel(II) 5,10,15,20-tetraphenyl-21,23-dioxaporphyrin dichloride $(O_2TPP)Ni^{II}Cl_2$ (**1**-Cl, Chart 1). The paramagnetic nickel(II) ion of **1**-Cl is located in the plane of the macrocycle and two chloride anions occupy axial positions. To search for the novel paramagnetic organonickel(II) species, bearing two σ-phenyls, we have investigated the reaction of $(O_2TPP)Ni^{II}Cl_2$ with aryl-containing Grignard reagents, anticipating a simultaneous replacement of two chloride ligands by two phenyls, to yield surmised $(O_2TPP)Ni^{II}(Ph)_2$. To the best of our knowledge, these investigations present the first identification of a paramagnetic organonickel(II) complex containing two σ-bound aryl ligands.

Results and Discussion

Addition of aryl-containing Grignard reagents [PhMgCl, PhMgBr, (Ph-d_5)MgBr, (*o*-MePh)MgBr, (*m*-MePh)MgBr] dissolved in ethyl ether or THF to the toluene-d_8 solutions (203 K) of $(O_2TPP)Ni^{II}Cl_2$ (**1**-Cl), $(O_2TPP\text{-}d_4)Ni^{II}Cl_2$ (**1**-d_4-Cl, deuterated in all pyrrole positions), or $(O_2TPP)Ni^{II}Br_2$ (**1**-Br) resulted in formation of a variety of paramagnetic organonickel species which have been detected and subsequently characterized by ^{1}H and ^{2}H NMR (Figure 1, Table 1). To obtain appropriate insight into the general relation between the ^{1}H NMR pattern of $(O_2TPP)Ni^{II}X_2$ and the nature of ligations in addition to the σ-phenyl coordination, some other axial ligands have been investigated. The axial ligands have been judiciously selected to cover a wider scope of σ and π donor/acceptor properties, thus X equals Br^-, CN^-, pyridine, and phenoxide (Table 1).

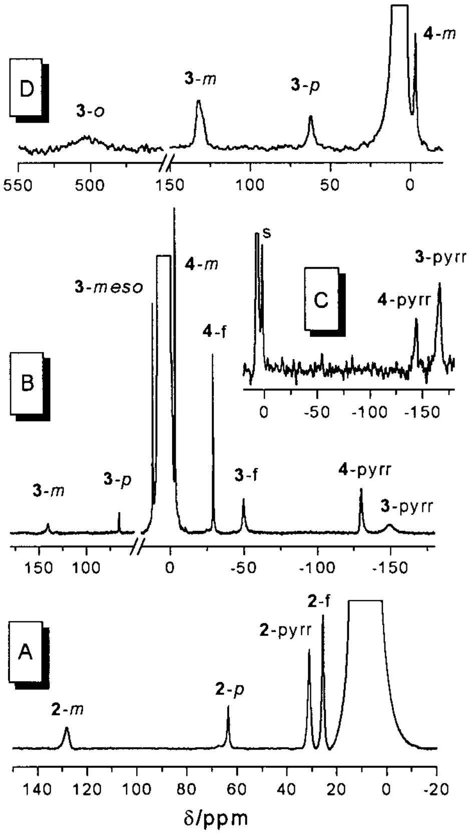


Figure 1. NMR spectra of the arylated nickel(II) 21,23-dioxaporphyrin. ^{1}H NMR in toluene-d_8: (A) $(O_2TPP)Ni^{II}(Ph)Cl$, **2**, 243 K; (B) mixture of $(O_2TPP)Ni^{II}(Ph)Br$, **3**, and $(O_2TPP)Ni^{II}(Ph)_2$, **4**, 263 K. ^{2}H NMR in toluene: (C) $(O_2TPP\text{-}d_4)Ni^{II}(Ph)Br$, **3**-$d_4$, and $(O_2TPP\text{-}d_4)Ni^{II}(Ph)_2$, **4**-$d_4$ (deuterated in all pyrrole positions), 243 K; (D) $(O_2TPP)Ni^{II}(Ph\text{-}d_5)Br$, **3**-$d_5$, and $(O_2TPP)Ni^{II}(Ph\text{-}d_5)_2$, **4**-$d_5$, 263 K. Assignments: (macrocycle protons) pyrr, pyrrole, *f*, furan, *meso*, *meso*-phenyls; (σ-aryl protons) *m*, meta, *p*, para.

Typically the resonance assignments have been made on the basis of relative intensities, line width analysis, and the site-specific deuteration or methylation (Figures 1 and 2). Consequently in each case the stoichiometry of the σ-phenyl adducts has been unambiguously determined by a careful comparison of resonance intensities assigned to the macrocycle (pyrrole and furan) and σ-aryl (ortho, meta, and para) protons, respectively.

The stoichiometry and the spectral pattern of the formed complexes depend strongly on the counteranion in the Grignard reagent. Addition of PhMgCl to **1**-Cl (203 K) led to the substitution of only one chloride ligand by the phenyl anion, yielding $(O_2TPP)Ni^{II}(Ph)Cl$ (**2**). The ^{1}H NMR spectral characteristic (Figure 1, trace A) and accordingly the electronic structure of the monoaryl complex **2** is similar to those of **1** and the related species formed in the thia-, *N*-methyl-,[13] oxa-, and selenaporphyrin[14] paramagnetic organonickel(II) series. There are two downfield resonances that have been assigned to the equatorial ligand (31.53 ppm (pyrr), 25.85 ppm (furan)). Additionally two other resonances appear at 129.2 and 63.7 ppm (203 K) that can be assigned to meta and para protons of the σ-coordinated phenyl. The positions of phenyl resonances are in the limits determined for the σ-phenylnickel(II) derivatives

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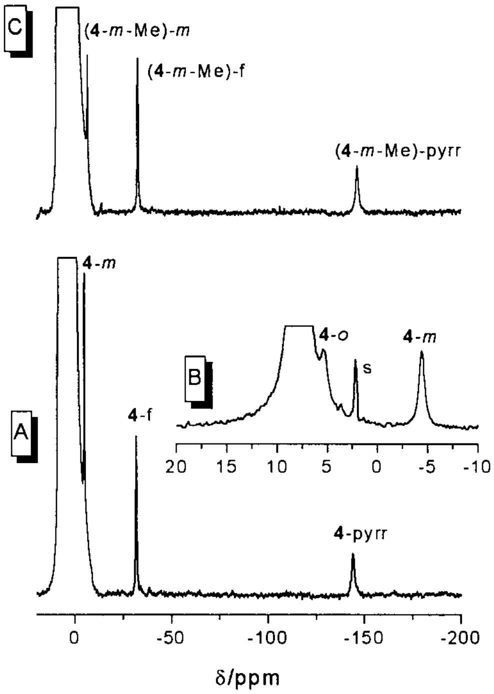

Figure 2. NMR spectra of the arylated nickel(II) 21,23-dioxaporphyrin (243 K). (A) $(O_2TPP)Ni^{II}(Ph)_2$, **4**; (C) $(O_2TPP)Ni^{II}$(*m*-MePh)$_2$, **4**-*m*-Me (^{1}H NMR in toluene-d_8); (B) $(O_2TPP)Ni^{II}(Ph\text{-}d_5)_2$, **4**-$d_5$ (^{2}H NMR in toluene). Assignments: (macrocycle protons) pyrr, pyrrole, f, furan; (σ-aryl protons) *o*, ortho, *m*, meta, s, solvent.

in the high-spin electronic state $(d_{xy})^2(d_{xz})^2(d_{yz})^2(d_{z^2})^1(d_{x^2-y^2})^1$ revealed previously for nickel(II) monoheteroporphyrins. Thus **2** can be formulated as a nickel(II) 21,23-dioxaporphyrin complex containing one σ-phenyl and one chloride ligand in a trans-arrangement. On the other hand, the addition of PhMgBr in ether or THF to the toluene solution of **1**, kept at low temperature, resulted in formation of a different monophenyl adduct **3** tentatively assigned as $(O_2TPP)Ni^{II}(Ph)Br$ and a remarkable bisphenyl adduct $(O_2TPP)Ni^{II}(Ph)_2$ (**4**) (Figure 1, trace B). The molar ratio of **3** and **4** depends on an array of factors introduced by experimental conditions, such as temperature, substituents on the aryl ring, anions present in the Grignard reagent and in the starting dihalo complex **1**, or solvent added along with the aryl carboanion. Titration of **1**-Br with PhMgBr or (*m*-MePh)MgBr added as a diethyl ether solution generated only the bisaryl species **4** which was observed in the 203−263 K temperature range (Figure 2). Addition of (*o*-MePh)MgBr in diethyl ether to the toluene solution of **1**-Br resulted in an exclusive formation of the monoaryl compound **3**-*o*-Me which was detected below 233 K. Titration of **1**-Br with the Grignard reagent in THF takes a course different from that observed for the same Grignard reagent but dissolved in diethyl ether. For instance, the addition of PhMgBr in THF produces the mixtures of **3** and **4**. The molar ratio of **3** to **4** depends on the temperature of the sample, and this value increases at higher temperature. Comparison of the ^{1}H NMR spectra collected in the course of the systematic titration of **1**-Cl with PhMgBr in THF reveals the fact that the molar ratio of mono- and bisadduct is not to be affected by the total concentration of carboanion. Accordingly, the molar ratio of mono- to bisadduct equals 1.2:1 at 203 K in the range of 0.5−30 equiv of the Grignard reagent added. However this value changed to 2:1 once the temperature was increased to 243 K. The reaction of **1**-Cl with PhMgBr (ethyl ether) has been also examined. In this system both organonickel(II) compounds are simultaneously formed with clear preference for the bisphenyl one. The molar ratio of **3** to **4** varied from ca. 1:10 at 203 K to 1:5 at 243 K.

Both species **3** and **4** have demonstrated the ^{1}H NMR patterns without a parallel to any nickel(II) porphyrin or heteroporphyrin.[12−17] The mono- and the bisaryl adducts show their pyrrole and furan resonances shifted strongly upfield. Sharing the spectral pattern for the 21,23-dioxaporphyrin protons, they differ substantially in positions of the axial phenyl resonances. The ortho, meta, and para proton resonances are located in the low-field part of the spectrum of **3** (Figure 1, traces B and C) and are spread over the enormous region of 500−20 ppm, analogously to **2** or to other σ-aryl nickel(II) monoheteroporphyrin complexes.[13,14] In contrast, the phenyl signals of **4** have been detected in the strikingly narrow domain (8 to −10 ppm, Figure 2, trace B). Still, a differentiation of the chemical shifts as well as the number and intensities of the corresponding resonances definitely indicates coordination of two equivalent η^1-phenyl ligands. In particular, the paramagnetic upfield-shifted (−8.3 ppm, 203 K; −3.0 ppm, 263 K) signal of meta protons of the σ-coordinated phenyl is well-separated from the crowded "diamagnetic" region of the spectra that allows a direct comparison of integrated peak intensities. The *meta*-phenyl and β-furan resonances have been considered, as they are closely located and demonstrate similar line widths. They reveal identical intensities that unambiguously indicate the 2:1 phenyl to nickel(II) 21,23-dioxaporphyrin stoichiometry.

Warming of **2**, **3,** or **4** resulted in their decomposition, so the corresponding ^{1}H NMR spectra could not be detected at room temperature. The process yields new species that demonstrate EPR signals related to one-electron reduction products of the nickel(II) 21,23-dioxaporphyrins (Figure 3).[15] Comparison of EPR intensities of the reduced species with that of the external standard (a stable radical TEMPO), determined by the double integration, reveals that they constitute the major decomposition products. The anisotropy of the **g** tensor and the values of components indicate a metal-centered reduction rather than an alternative anion radical formation.[18−20] However, the spin Hamiltonian parameters differ significantly from those reported for $(O_2TPP)Ni^{I}Cl$[15] or obtained for $(O_2TPP)Ni^{I}Cl$ or $(O_2TPP)Ni^{I}Br$ (**5**) generated by reduction of $(O_2TPP)Ni^{II}Cl_2$ or $(O_2TPP)Ni^{II}Br_2$, respectively, with zinc amalgam in the presence of potentially coordinating solvents (Et_2O, THF) (Table 2, Figure 3). The EPR parameters are determined by the σ-aryl and the oxygen coordinating solvent available in the reaction mixture but not by the halogenide anions. The same spectral parameters were found for decomposition products of phenyl adduct obtained in the systems **1**-Cl−PhMgBr(Et_2O), **1**-Br−PhMgBr(Et_2O), and **1**-Cl−PhMgCl(Et_2O), although in the latter case an admixture of **5** was also detected. Different spectra were obtained for the thermal decomposition products of $(O_2TPP)Ni^{II}(Ph)_2$ and $(O_2TPP)Ni^{II}$(*m*-MePh)$_2$, even though both were

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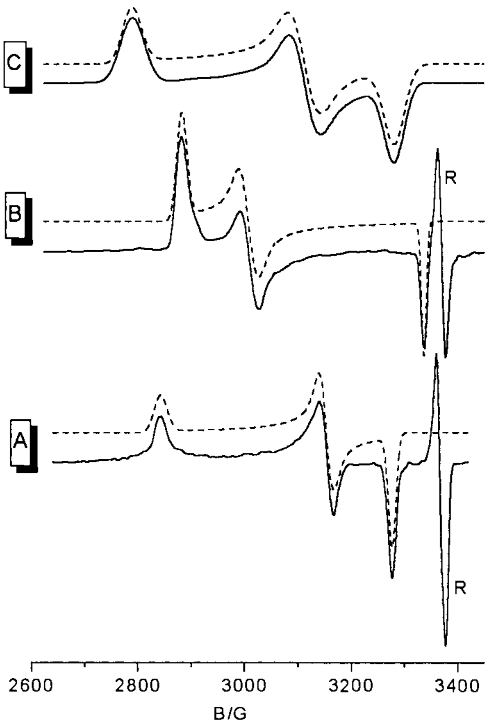

Figure 3. EPR spectra of nickel(I) 21,23-dioxaporphyrin complexes in frozen toluene solutions (77 K): (A) $(O_2TPP)Ni^IBr$, **5**, reduction product of $(O_2TPP)Ni^{II}Br_2$, **1**-Br, with zinc amalgam in toluene with 1% of THF; (B) $(O_2TPP)Ni^I(Ph)$, **6**, obtained in the system **1**-Br−PhMgBr−Et_2O; (C) **6** obtained in the system **1**-Br−PhMgBr−THF. Solid lines, experimental spectra; dashed lines, best fits of simulated spectra. R denotes signal of free radical formed in small quantities upon reduction.

Table 2. EPR Parameters of $(O_2TPP)Ni^I(X)(Solv)$ in Frozen Toluene Solutions at 77 K

X	solv	g_1	g_2	g_3
Ph^-	THF	2.411	2.161	2.049
Ph^-	Et_2O	2.342	2.245	2.024
o-$MePh^-$	Et_2O	2.346	2.113	2.022
m-$MePh^-$	Et_2O	2.326	2.232	2.024
Cl^- [a]	−	2.298	2.140	2.093
Br^-	−	2.344	2.139	2.086
Br^-	THF	2.373	2.139	2.059

[a] Data from ref 15.

obtained with the same halogenide/solvent composition (Br^-/Et_2O). Consequently the products of decomposition can be described as σ-phenylnickel(I) 21,23-dioxaporphyrin $(O_2TPP)Ni^I(Ph)$, **6**, or σ-(*meta*-tolyl)nickel(I) 21,23-dioxaporphyrin $(O_2TPP)Ni^I$(*m*-MePh), **6**-(*m*-Me), coordinating optionally one oxygen-donating solvent molecule (THF or ether). In a separate experiment we have verified its formation by reacting $(O_2TPP)Ni^IBr$ with the Grignard reagent. A resemblance of the EPR spectra generated by two different routes indicated indeed that the same organonickel(I) species **6** has been detected. The unstable $(O_2TPP)Ni^I(Ph)$ species constitutes an uncommon example of a d^9 organometallic complex.[20] The likely route to generate **6** is a homolytic cleavage of one of the two nickel−carbon bonds in the bisaryl adduct **4**. A stepwise mechanism which involves cleavage of the Ni−C bond of **2** or **3** to produce **5**, i.e., $(O_2TPP)Ni^ICl$ or $(O_2TPP)Ni^IBr$, respectively, followed by arylation with excess Grignard reagent accounts for the production of **6** as well. An indication of such a path is the formation of both **5** and **6** observed during the decomposition of **2** or **3**-*o*-Me. The overall transformation routes of **1**-Cl in the course of reaction with Grignard reagents are summarized in Scheme 1.

The origin and direction of the isotropic shift in organonickel(II) 21,23-dioxaporphyrins has been also a matter of interest.[15,21] Generally, a straightforward and unambiguous correlation between the NMR pattern and the molecular and electronic structure has been determined for paramagnetic metalloporphyrins[16,22] including nickel(II) heteroporphyrins and porphyrins.[12−17] Accordingly, the protons of the nickel-bound phenyl display substantial downfield contact shifts which are indicative of the σ-contact contribution. The isotropic shifts of the equatorial macrocycles are also dominated by the same effect, revealing resonances in the 0−60 ppm region. The general examination of the isotropic shift for low-spin iron(III) and iron(IV) tetraarylporphyrins[23] as well as ruthenium(IV) octaethylporphyrin[24] indicated the large π-spin density at the axial phenyl ligand although some contribution of the σ-mechanism was also suggested.[13] The phenyl pattern of **4** escapes any direct comparison as the bis(σ-phenyl) derivatives of metalloporphyrins, reported till now, are diamagnetic.[24,25]

Thus the peculiar spectral features of **3** and **4** indicate a profound alteration of the electronic structure of nickel(II) ion upon coordination of phenyl ligand(s) (Figure 1, Table 1). The upfield positions of the macrocycle signals imply domination of a spin delocalization mechanism that involves the π-orbital framework.[16,22] Hence, the nickel(II) d orbitals, contributing to the single occupied molecular orbitals, must be those of π-symmetry, i.e., d_{xz} and d_{yz}. Additionally, the relatively small isotropic shifts of the aryl protons, determined for **4,** imply the low effectiveness of the spin density delocalization in the carbon−nickel bond directions. An interpretation of this spin delocalization requires a change of the metal ion ground state from $(d_{xy})^2(d_{xz})^2(d_{yz})^2(d_{z^2})^1(d_{x^2-y^2})^1$ that is common for all five- and six-coordinated high-spin nickel(II) macrocycles, including the aryl monoadduct **2**, to the $(d_{xy})^2(d_{x^2-y^2})^2(d_{yz})^2(d_{z^2})^1(d_{xz})^1$ and $(d_{xy})^2(d_{x^2-y^2})^2(d_{z^2})^2(d_{yz})^1(d_{xz})^1$ configurations for **3** and **4**, respectively. Such a profound electronic transformation cannot be accounted for merely by a choice of σ- or π-donating properties of the aryl ligand, keeping in mind the qualitative difference of spectral patterns determined for the two monoadducts **2** and **3**. This opinion is supported by a rather moderate influence of the axial ligation on the furan and pyrrole resonance positions despite the marked difference of ligand properties (Table 1). Thus a viable hypothesis has been considered which invokes a *cis*-coordination of two monodentate ligands (phenyl and bromine anions for **3** and two aryls for **4**) accompanied by a displacement of the nickel ion from the plane defined by the macrocycle. The profound structural rearrangement with respect to the more typical *trans*-coordination might be a sufficient

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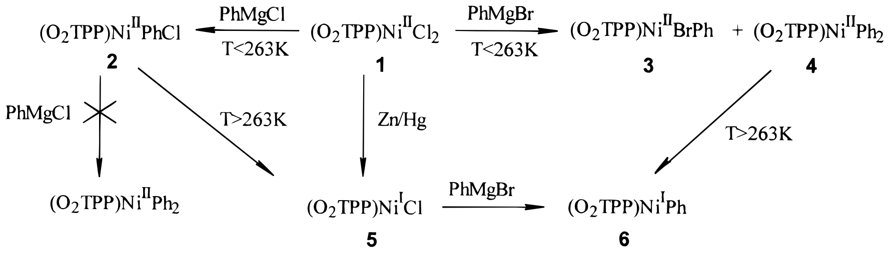
Scheme 1



reason to modify the ground electronic state allowing for the determined spin density distribution. The *cis*-configuration of two monodentate ligands or a single bidendate ligand, although less common, was observed for nickel(II) tetraaza macrocyclic complexes[26] and for selected cases of metalloporphyrin chemistry.[25,27] In particular, both *cis*- and *trans*-bis(σ-phenyl) adducts were characterized recently for tin(IV) tetraphenylporphyrin.[25c]

In conclusion, a core modification of porphyrin by introduction of two oxygen atoms seems to be crucial in relative stabilization of the unprecedented organometallic derivatives of nickel(II) and nickel(I). A neutral character of the equatorial ligand, imposing a need for one (Ni^I) or two (Ni^{II}) anionic ligands to compensate the overall molecule charge, seems to be instrumental in the stoichiometry determination of organonickel species trapped at low temperature.

Experimental Section

Materials. 5,10,15,20-Tetraphenyl-21,23-dioxaporphyrin and its nickel(II) complexes were synthesized as described recently.[15]

Instrumentation. ^{1}H (300 MHz) and ^{2}H NMR (46 MHz) spectra were measured 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 induced typically 25-Hz broadening. The peaks were referenced against solvent resonances. EPR spectra were obtained with an ESP 300E spectrometer. The magnetic field was calibrated with a proton magnetometer and the EPR manganese standard. The EPR spectra were simulated assuming orthorhombic symmetry.

Sample Preparation. A sample of 3 mg of nickel(II) 21,23-dioxaporphyrin was dissolved in 0.5 cm^3 of oxygen-free toluene-d_8 directly in an NMR tube capped with a rubber septum. The sample was cooled to 193 K in the acetone slush bath, and the Grignard reagent was titrated into the NMR tube using a syringe. The sample was shaken vigorously and then immediately transferred to an NMR spectrometer which was maintained at 203 K. Samples of the reduced nickel 21,23-dioxaporphyrin complexes for the EPR measurements were prepared by stirring with the suspension of fine-powdered zinc amalgam for 2 h under inert atmosphere. The reducing reagent was then removed by filtration, and the filtrate was used as a stock solution.

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