Reactions of nickel(II) 2,21-dimethyl-2-aza-21-carbaporphyrin with phenyl Grignard reagents, phenyllithium, and *n*-butyllithium.

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Streszczenie

Addition of a phenyl Grignard reagent to a toluene solution of the nickel(II) chloride complex of a dimethylated inverted porphyrin, (2-NCH_3-21-CH_3CTPP)Ni^{II}Cl (**1**), at 203 K results in the formation of a rare paramagnetic (σ-phenyl)nickel(II) species, (2-NCH_3-21-CH_3CTPP)Ni^{II}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-NCH_3-21-CH_3CTPP)Ni^{II}Ph (**2**). One-electron reduction with excess PhLi yields [(2-NCH_3-21-CH_3CTPP)Ni^{II}Ph]$^-$ (**3**), which can be also generated by independent routes, e.g., by reduction of (2-NCH_3-21-CH_3CTPP)Ni^{II}Ph using lithium triethylborohydride or tetrabutylammonium borohydride. The spectroscopic data indicate that (2-NCH_3-21-CH_3CTPP)Ni^{II}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-NCH_3-21-CH_3CTPP)NiBu]$^-$ or [(2-NCH_3-21-CH_3CTPP)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)).

Słowa kluczowe

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