Organonickel complexes of 21,23-dioxaporphyrin. Identification of the paramagnetic organononickel(II) complex with two η^1-phenyl ligands.

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Streszczenie

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(2)TPP), 1, at 203 K resulted in formation of a variety of rare paramagnetic sigma-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(2)TPP)Ni(II)(Ph)Cl (2). The coordination of a sigma-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(2)TPP. Titration with PhMgBr resulted in formation of the different monophenyl adduct (O(2)TPP)Ni(II)(Ph)Br (3) and the first paramagnetic organonickel(II) complex with two sigma-aryl ligands, i.e., the bisphenyl adduct (O(2)TPP)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 sigma-phenylnickel(I) 21,23-dioxaporphyrin (O(2)TPP)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(2)TPP)Ni(I)Br with the Grignard reagent.

Adres publiczny

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