Reactions of nickel(II) 2-aza--5,10,15,20-tetraphenyl-21-carbaporphyrin with methyl iodide. The first structural characterization of a paramagnetic organometallic nickel(II) complex.

Autorzy

Piotr J. Chmielewski

Lechosław Latos-Grażyński

Tadeusz Głowiak

Rok wydania

1996

Czasopismo

Journal of the American Chemical Society

Numer woluminu

118

Strony

5690-5701

DOI

10.1021/ja9527028

Kolekcja

Naukowa

Język

Angielski

Typ publikacji

Artykuł

Streszczenie

The methylation of a nickel(II) complex (CTPP)Ni^{II} of 2-aza-5,10,15,20-tetraphenyl-21-carbaporphyrin ($CTPPH_2$) with the mild methylating agent methyl iodide yields novel stable organonickel(II) complexes: diamagnetic (21-CH_3TPP)Ni^{II} and two scarce paramagnetic species (2-NH-21-CH_3CTPP)Ni^{II}X and (2-NCH_3-21-CH_3CTPP)Ni^{II}X (X = Cl, I). The demetalation procedure resulted in isolation of two 21-carbaporphyrin derivatives, methylated at the internal C(21) carbon atom, i.e., 2-aza-5,10,15,20-tetraphenyl-21-methyl-21-carbaporphyrin (21-CH_3-$CTPPH_2$) and 2-aza-2-methyl-5,10,15,20-tetraphenyl-21-methyl-21-carbaporphyrin (2-NCH_3-21-CH_3CTPPH). The methylation mechanism involves the oxidative addition of the methyl cation to the carbaporphyrin C(21) activated due to Ni−C coordination. These C-methylated macrocycles preserve their coordinating properties as the remetalation processes have been carried out. The reversible concerted addition of HX converts the diamagnetic (21-CH_3TPP)Ni^{II} into the paramagnetic (2-NH-21-CH_3CTPP)Ni^{II}X. The axial coordination step is accompanied by a protonation of the peripheral nitrogen. The structures of (21-CH_3CTPP)NI^{II} (monoclinic, $P2_1/c$; a = 15.055(3) Å, b = 15.795(3) Å, c = 17.069(3) Å, β = 115.00(3)°, Z = 4, least-square refinement of 476 parameters using 3622 reflections, R = 0.069) and (2-NCH_3-21-CH_3CTPP)Ni^{II}I (monoclinic, $P2_1/n$; a = 12.946(3) Å, b = 23.519(5) Å, c = 13.945 Å; β = 93.2(3)°, Z = 4, the least-square refinement of 502 parameters using 3257 reflections, R = 0.0559) have been determined by X-ray diffraction. In the first case the nickel(II) is four-coordinate with bonds to three pyrrole nitrogen atoms (Ni−N distances 1.948(5); 1.955(5); 1.938(5) Å) and the pyrrole carbon (Ni−C 2.005(6) Å). The nickel lies in the plane of the three nitrogens, while the methylated pyrrole is sharply tilted out of the plane with dihedral angle between the

plane of three nitrogens and the methylated pyrrole plane being −42.2°. The methylated pyrrole is bound to nickel *via* a pyramidal carbon in the η^1-fashion. The first structurally characterized paramagnetic organonickel(II) complex (2-NCH_3-21-CH_3CTPP)Ni^{II}I presents unique features related to its electronic structure. The nickel(II) is five-coordinate with bonds to three pyrrole nitrogen atoms (Ni−N distances 2.032(8); 2.057(8); 1.979(8) Å) and to the pyrrole C(21) carbon (Ni−C 2.406(9) Å). The nickel is moved out from the plane of the three nitrogen plane toward the iodide ligand. The 21-CH_3 group and iodide are located on the opposite sides of the macrocycle. The substituted pyrrole is sharply tilted out of the plane with the dihedral angle between the three nitrogen plane and the methylated pyrrole plane being −55.3°. The methylated pyrrole is bound to nickel in the η^1-fashion but the coordinating C(21) atom preserves features related to trigonal sp^2 hybridization. The angle between the inverted pyrrole plane and the Ni−C bond increases from 42.8° to 70.1° on moving from the diamagnetic to paramagnetic species. The ^{1}H NMR and ^{2}H NMR spectra of paramagnetic (2-NH-21-CH_3CTPP)Ni^{II}X and (2-NCH_3-21-CH_3CTPP)Ni^{II}X complexes have been examined. Functional group assignments have been made with use of selective deuteration and 2D COSY experiments. The characteristic patterns of six downfield shifted pyrrole resonances accompanied by upfield shifted 3-H and 2-NH resonances are diagnostic of C-methylation. The 21-CH_3 resonance appears in a characteristic 90−110 ppm region.

Słowa kluczowe

Alkyls, Ligands, Organic reactions, Phenyls, Pyrroles

Adres publiczny

https://doi.org/10.1021/ja9527028

Strona internetowa wydawcy

https://www.acs.org/content/acs/en.html