EPR and ^{2}H NMR studies on the oxidation of nickel(II) tetraphenylcarbaporphyrin to form novel organometallic nickel(III) complexes.

Autorzy

Piotr J. Chmielewski

Lechosław Latos-Grażyński

Rok wydania

1997

Czasopismo

Inorganic Chemistry

Numer woluminu

36

Strony

840-845

DOI

10.1021/ic9608760

Kolekcja

Naukowa

Język

Angielski

Typ publikacji

Artykuł

Streszczenie

One-electron oxidation of nickel(II) 5,10,15,20-tetraaryl-2-aza-21-carbaporphyrin ((CTPP)Ni^{II}) and nickel(II) 2-methyl-5,10,15,20-tetraaryl-2-aza-21-carbaporphyrin ((MeCTPP)Ni^{II}) resulted in formation of rare organonickel(III) derivatives. The half-wave potential for the first oxidation of (CTPP)Ni^{II} and (MeCTPP)Ni^{II} equals 0.66 V and 0.72 V, respectively (*vs* SCE, CH_2Cl_2 solution, TBAP). The EPR spectral patterns of the one-electron-oxidized species have been determined at 293 and 77 K. In both temperatures the spectral parameters markedly depend on the axial ligand introduced by oxidants or in methathesis. In each case the spin-Hamiltonian parameters (g_{av} > 2.1 (77 K) org_{iso} > 2.1 (293 K)) reveal a metal-centered oxidation rather than a cation radical formation (g_{iso} ≈ 2.002). The localization of the one-electron oxidation on the nickel ion has been supported by the observation of ^{61}Ni hyperfine splitting. The ^{2}H NMR investigations, carried out for pyrrole deuterated derivatives: (CTPP-d_7)Ni^{III}Br, (CTPP-d_7)Ni^{III}(NO_3), and (Me-d_3-CTPP)Ni^{III}OH, confirmed independently by the nickel(III) electronic structure.

Słowa kluczowe

Electron paramagnetic resonance spectroscopy, Ligands, Macrocycles, Oxidation, Pyrroles

Adres publiczny

https://doi.org/10.1021/ic9608760

Strona internetowa wydawcy

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