Formation and reactivity of paramagnetic organometalic nickel complexes of 21-oxa and 21-selenaporphyrins - ^{1}H NMR and EPR investigations.

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Streszczenie

Addition of aryl Grignard reagents to a toluene solution of nickel(II) monohalide complexes of 5.20-bis(*p*-tolyl)-10.15-diphenyl-21-oxaporphyrin (ODTDPPH) and 5.20-diphenyl-10.15-bis(*p*-tolyl)-21-selenaporphyrin (SeDPDTPH) at 203 K resulted in formation of paramagnetic σ-aryl nickel(II) derivatives which were identified and characterized by means o f ^{1}H NMR. The coordination of the aryl ligand has been unambiguously proven by the unique downfield pattern of the corresponding resonances. The (σ-aryl)nickel(II) derivatives are in the high-spin electronic state: $(d_{xv})^2(d_{vz})^2(d_{vz})^2(d_{z^2})^2(d_{z^2})^1(d_{x^2-y^2})^1$. A homolytic cleavage of the Ni^{11}-C bond has been determined for (ODTDPP)Ni^{II}(Ar) and (SeDPDTP)Ni^{II}(Ar) in toluene with formation of low-valent nickel species: (ODTDPP)Ni and (SeDPDTP)Ni. One-electron reduction of (SeDPDTP)Ni^{II}Cl to generate (SeDPDTP)Ni has been investigated by means of EPR, involving ^{61}Ni isotope enrichment and spectral simulations. A considerable increase in metal d-orbital contribution to the singly occupied molecular orbital has been observed upon coordination of 1-methylimidazole to (SeDPDTP)Ni.

Słowa kluczowe

Nickel complexes, Paramagnetic complexes, Selenaporphyrin complexes

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