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Paramagnetic σ-bonded phenylnickel(II) macrocyclic systems. Nuclear magnetic resonance identification of (σ-phenyl)nickel(II) 5,20-diphenyl-10,15-bis(*p*-tolyl)-21-thiaporphyrin and (σ-phenyl)nickel(II) *N*-methyltetraphenylporphyrin.

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Streszczenie

Addition of the phenyl Grignard reagent to toluene or dichloromethane solutions of nickel(II) monohalide complexes of 5,20-diphenyl-10,15-bis(p-tolyl)-21-thiaporphyrin(SDPDTPH) and iV-methyltetraphenylporphyrin (NCH3TPPH) at 70^{0}C resulted in formation of paramagnetic (ff-phenyl) nickel (II) derivatives which were characterized by means of NMR and* 12 HNMR. The coordination of the phenyl ligand has been proven by the unique downfield pattern of three phenyl resonances in the respective 2HNMR spectra of(SDPDTP)Nin(C6D5)(1)and(NCH3-TPP)Nin(C6D5)(2) (1,ortho616,meta170.0,para76.0;2,ortho568,metal148.0,para62.8 70^o C ,in ppm vs TMS in toluene). The^-phenyl)nickel(II)derivativesareinthehigh-spin paramagnetic electronic state:d^d^d^d^d*^,.The protons of the nickel-bound phenyl group display substantial hyperfme shifts which are dominated by the -contact contribution A contact shift patterne stablished for pheny lligand resembles that of pyridine in a large variety of nickel(II) pyridine complexes as both ligands are isoelectronic. A homolytic cleavage of the Nin-C bond has been observed for (SDPDTPjWfCeHs) in toluene with formationo f(SDPDTP)Ni1.The decomposition of (NCH3TPP)Nin(C6H5)in toluene results in formation of (TPP)Ni11,dueto the demethylation.

Adres publiczny

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