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^{1}H nuclear magnetic resonance studies of the reaction of iron(III) porphyrin cation radical with aryl Grignard reagents.

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Streszczenie

Addition of aryl Grignard reagents to an iron(III) tetraphenylporphyrin π cation radical, [(TPP·)Fe^{III}Cl] ($SbCl_6$), in dichloromethane solution at 202 K yields a mixture of σ-phenyl iron(IV) tetraphenylporphyrin, [(TPP)Fe^{IV}(Ph)] ($SbCl_6$), and σ-phenyl iron(III) tetraphenylporphyrin, (TPP)Fe^{III}Cl. A σ-phenyliron(III) complex is also formed by nucleophilic addition to the tetraphenylporphyrin macrocycle accompanied by σ-phenyl axial coordination. The complexes formed were identified by ^{1}H NMR spectroscopy. A new route for generating σ-aryl iron(IV) porphyrin species from the iron(III) porphyrin π cation radical was established. The characteristic ^{1}H NMR pattern of the low-spin iron(III) porphyrin ring modified species reflects its C_s symmetry and includes four upfield-shifted pyrrole resonances (2.31, −10.40, 20.39 and −20.87 ppm, 202 K) accompanied by a set of σ-phenyl resonances (*ortho*, −188.4; *p*-H, −102.5; *p*-CH_3 for σ-*p*-tolyl, 162.3 ppm). Analysis of the paramagnetic shifts of the σ-phenyl (σ-*p*-tolyl) ligand of the new species indicates a high π spin density consistent with the electronic structure of low-spin iron(III) and the contribution of a σ-delocalization mechanism via donation from a filled σ-phenyl orbital to an empty d_{z2}; orbital. The formation of a low-spin σ-phenyliron(III) isoporphyrin or low-spin σ-phenyl *N*-arylporphyrin is considered. The *meso* substitution can be accounted for by a mechanism which emphasizes the radical nature of the reaction substrate and involves the formation of σ-transient forms.

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