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Nuclear magnetic resonance studies of the formation of tertiary alkyl complexes of iron(III) porphyrins and their reactions with dioxygen.

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Iron(III) complexes of tetra-(p-tolyl)porphyrin (TTPH2) with axial adamantyl (1-ad), camphane (4-cam), and zerz-butylv ligands have been prepared and characterized by NMR spectroscopy. These have typical properties for low-spin (S = 1 /2), five-coordinate complexes. Analyses of the paramagnetic NMR spectral patterns for a variety of axial ligands are made and compared with those of aliphatic amines. These spectra exhibit sizeable dipolar shifts and can show non-Curie temperature dependence, particularly for the ^-protons. Treatment of TTPFem(4-cam), TTPFem(l-ad), or TTPFem(r-Bu) with dioxygen in toluene at -70 °C produces a mixture of TTPFeM1OH, TTPFemOFelllTTP, and TTPFe,luOOR (R = Zerz-butyl, 4-cam, or 1-ad). The absence of hydrogen atoms in the -carbon of these tertiary alkyl peroxide complexes alters their reactivity so that an intermediate formed by the 0-0 bond-breaking step can be detected. Treatment of TTPFemOO(4-cam) with pyridineat -70 °C results in its conversion into TTPFelv=0 through homolysis of the 0-0 bond.

Adres publiczny

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