Ruthenium(II) and ruthenium(III) complexes of *p*-benziporphyrin: merging equatorial and axial organometallic coordination.

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Streszczenie

A diamagnetic ruthenium(II) complex of 5,10,15,20-tetraphenyl-p-benziporphyrin [Ru^{II}(p-BzP)(CO)Cl] was obtained via the insertion of ruthenium into p-benziporphyrin using triruthenium(0) dodecacarbonyl [$Ru_3(CO)_{12}$] as the metal source. The procedure applying dichloro(cycloocta-1,5-diene)ruthenium(II) (polymer, [$Ru(COD)Cl_2]_n$) afforded the paramagnetic six-coordinate ruthenium(III) p-benziporphyrin [Ru^{III}(p-BzP)Cl_2]. As shown by X-ray crystallography, the p-phenylene ring in both complexes is sharply tilted out of the N_3 plane, as reflected by the respective N_3 (pyrrole)-C_6 (p-phenylene) dihedral angle [Ru^{II}(p-BzP)(CO)Cl, 52.5°; Ru^{III}(p-BzP)Cl_2, 53.7°]. p-Phenylene is bound to the ruthenium cation in an η^2 fashion, revealing the shortest ever Ru-C distance in the series of p-benziporphyrin complexes [Ru^{II}(p-BzP)(CO)Cl, 2.275(2) Å; Ru^{III}(p-BzP)Cl_2, 2.324(5) Å]. The reaction of Ru^{II}(p-BzP)(CO)Cl with ArMgCl or AlkMgCl results in the formation of diamagnetic six-coordinate ruthenium(II) p-benziporphyrin complexes containing the apically coordinated σ-alkyl or σ-aryl ligands, where the metal ion simultaneously coordinates to three carbon centers respectively accommodating η^2 (phenylene) and σ (aryl and alkyl) modes. Reactions of σ-aryl (alkyl) carbanions with paramagnetic Ru^{III}(p-BzP)Cl_2 have been followed by ^{1}H NMR spectroscopy. The procedure afforded the six-coordinate paramagnetic ruthenium(III) p-benziporphyrin [Ru^{III}(p-BzP)(Ph)Cl], which binds one σ-aryl ligand, as reflected by the characteristic ^{1}H NMR spectra spread within the +120 to -120 ppm range. Both paramagnetic complexes Ru^{III}(p-BzP)(Ph)Cl and Ru^{III}(p-BzP)(p-Tol)Cl are formed as a mixture of two stereoisomers differentiated by two nonequivalent locations of σ-aryl with respect to the puckered macrocyclic ring. The paramagnetic shifts of σ-aryls are indicative of π-spin delocalization patterns. Analysis of the contact shifts and parallel density functional theory calculations of the spin density distribution in Ru^{III}(p-BzP)Cl_2, Ru^{III}(p-BzP)(Ar)Cl, and Ru^{III}(p-BzP)(Alk)Cl reflect the features of the $d_{xy}^2(d_{xz}d_{yz})^3$ electronic ground state.

Adres publiczny

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