Palladium(II), ruthenium(II), and ruthenium(III) complexes of 23-thiaazuliporphyrin: the case of coordination-induced contraction.

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Rok wydania

2016

Czasopismo

Inorganic Chemistry

Numer woluminu

55

Strony

1758-1769

DOI

10.1021/acs.inorgchem.5b02684

Kolekcja

Naukowa

Język

Angielski

Typ publikacji

Artykuł

Streszczenie

5,10,15,20-Tetraaryl-23-thiaazuliporphyrin (SAz) was synthesized starting from nonfunctionalized azulene using a “1 + 3” method to be applied as a monoanionic macrocyclic ligand that provides a peculiar [CNSN] coordination cavity. An insertion of palladium(II) afforded the cationic $[Pd^{II}(SAz)]^+$, which readily undergoes the seven-membered ring contraction to form palladium(II) 23-thiabenzocarbaporphyrin [Pd(SBzC)] providing the first example of metal azuliporphyrinoid contraction. A reaction of SAz and a ruthenium source ($[RuCl_2(CO)_3]_2$, $[RuCl_2(p\text{-cymene})]_2$, or $[RuCl_2(cod)]$) yielded ruthenium(II) 23-thiaazuliporphyrin $[Ru^{II}(SAz)Cl(CO)]$. As shown by X-ray crystallography the thiophene ring in [Ru(SAz)Cl(CO)] is sharply tilted out of the plane of the two pyrrole nitrogen and carbon atoms being bound to the ruthenium through the pyramidal sulfur in the η^1 fashion. In solution, as demonstrated by variable-temperature ^1H NMR investigations, [Ru(SAz)Cl(CO)] exists as an equilibrium mixture of two isomers that are differentiated by the direction of thiophene folding (toward or outward of the axial chloride ligand). Apart of $[Ru^{II}(SAz)Cl(CO)]$, ruthenium(III) 23-thiaazuliporphyrin $[Ru^{III}(SAz)Cl_2]$ was obtained when $[RuCl_2(p\text{-cymene})]_2$ or $[RuCl_2(cod)]_n$ were used for insertion. The most characteristic ^1H NMR features of paramagnetic $[Ru(SAz)Cl_2]$ are negative isotropic shifts of resonances assigned to *meso*-aryl, azulene, and pyrrolic hydrogen atoms. The analysis of contact shifts and the parallel density functional theory calculations of spin density distribution documented that in $[Ru(SAz)Cl_2]$ the metal ion acquires the $d_{xy}^2(d_{xz}d_{yz})^3$ ground electronic state. This C_s symmetry complex has singly occupied d_{xz} or d_{yz} orbitals that are symmetrically unequivalent. The resulting two different spin density distributions, when merged, reflect the spectroscopic image with the very specific π-spin delocalization, also including the azulene moiety.