Rhodium-induced reversible C—C bond cleavage: transformations of rhodium(III) 22-alkyl-*m*-benziporphyrins.

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Streszczenie

The structurally prearranged carbaporphyrins 22-methyl- and 22-ethyl-m-benziporphyrins provide the platform stabilizing aromatic rhodium(III) 22-(μ-methylene-m-benziporphyrin) and rhodium(III) 22-(μ-ethylidene-m-benziporphyrin). An intramolecular conversion facilitated by the m-phenylene reactivity and observed for both aromatic complexes efficiently leads to rhodium(III) 21-(μ-methylene)-21-carbaporphyrin and rhodium(III) 21-(μ-ethylidene)-21-carbaporphyrin. The distinctive macrocyclic environment of rhodium(III) 21-carbaporphyrin created an opportunity to trap unique organometallic transformations of inner core substituents affording the fulvene-like bond pattern or the rearrangement to 21-vinyl substituent. The one-electron reduction of the rhodium(III) carbaporphyrin anion π-radical with a (dxy)2(dxz)2(dyz)2–(P.−) electronic configuration is demonstrated. The further process of reduction of paramagnetic species triggers the ethyl migration from carbon(22) to rhodium(III), affording the diamagnetic rhodium(III) meta-benziporphyrin containing the apically coordinated σ-ethyl ligand providing an example of reversible C(sp2)−C(sp3) bond cleavage.

Słowa kluczowe

carbaporphyrinoids, C-C bond activation, migration, reversible bond cleavage, rhodium

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