

Two Rhodium(III) Ions Confined in a [18]Porphyrin Frame: 5,10,15,20-Tetraaryl-21,23-Dirhodaporphyrin

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Streszczenie

Tetraaryl-21,23-dirhodaporphyrin and a series of related monorhodaporphyrins have been obtained by tellurium-to-rhodium exchange in a reaction of tetraaryl-21,23-ditelluraporphyrin with $[\text{RhCl}(\text{CO})_2]_2$. These organometallic metallaporphyrins contain rhodium(III) centers embedded in rhodacyclopentadiene rings, incorporated within the porphyrin frames. The skeletons of 21,23-dirhodaporphyrin and 21-rhoda-23-telluraporphyrin are strongly deformed in-plane from the rectangular shape typical for porphyrins, due to rhodium(III) coordination preferences, the large size of the two core atoms, and the porphyrin skeleton constrains. These two metallaporphyrins exhibit fluxional behavior, as studied by ^1H NMR and DFT, involving the in-plane motion and the switch of the rhodium center(s) between two nitrogen donors. A side product detected in the reaction mixture, 21-oxa-23-rhodaporphyrin, results from tellurium-to-oxygen exchange, occurring in parallel to the tellurium-to-rhodium exchange. The reaction paths and mechanisms have been analyzed. The title 21,23-dirhodaporphyrin contains a bridged bimetallic unit, Rh_2Cl_2 , in the center of the macrocycle, with two rhodium(III) ions lying approximately in the plane of the porphyrinoid skeleton. The geometry of the implanted Rh_2Cl_2 unit is affected by macrocyclic constrains.

Słowa kluczowe

fluxionality, metallacycles, porphyrinoids, rhodium, tellurium

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