Palladium vacataporphyrin reveals conformational rearrangements involving Hückel and Möbius macrocyclic topologies.

Autorzy

Ewa Pacholska-Dudziak

Janusz Skonieczny

Miłosz Pawlicki

Ludmiła Szterenberg

Zbigniew Ciunik

Lechosław Latos-Grażyński

Rok wydania

2008

Czasopismo

Journal of the American Chemical Society

Numer woluminu

130

Strony

6182-6195

DOI

10.1021/ja711039c

Kolekcja

Naukowa

Język

Angielski

Typ publikacji

Artykuł

Streszczenie

5,10,15,20-Tetraaryl-21-vacataporphyrin (butadieneporphyrin, an annulene-porphyrin hybrid) which contains a vacant space instead of heteroatomic bridge acts as a ligand toward palladium(II). The metal ion of square-planar coordination geometry is firmly held via three pyrrolic nitrogen atoms where the fourth coordination place is occupied by a monodentate ligand or by an annulene part of vacataporphyrin. The macrocycle reveals the unique structural flexibility triggered by coordination of palladium. The structural rearrangements engage the C(20)C(1)C(2)C(3)C(4)C(5) annulene fragment which serves as a linker between two pyrrolic rings of vacataporphyrin albeit the significant ruffling of the tripyrrolic block is also of importance. Two fundamental modes of interactions between the palladium ion and annulene moiety have been recognized. The first one resembles an η^2-type interaction and involves the C(2)C(3) unit of the butadiene part. Alternatively the profound conformational adjustments allowed an in-plane coordination through the deprotonated trigonally hybridized C(2) center of butadiene. The coordinated vacataporphyrin acquires Hückel or extremely rare Möbius topologies readily reflected by spectroscopic properties. The palladium vacataporphyrin complexes reveal Hückel aromaticity or Möbius antiaromaticity of [18]annulene applying the butadiene fragment of vacataporphyrin as a topology selector. The properties of specific conformers were determined using ^{1}H NMR and density functional theory calculations.

Słowa kluczowe

Palladium, Ligands, Butadiene, Molecular structure

Adres publiczny

https://doi.org/10.1021/ja711039c

Strona internetowa wydawcy

https://www.acs.org/content/acs/en.html