Reactivity of silole within a core-modified porphyrin environment: synthesis of 21-silaphlorin and its conversion to carbacorrole.

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Streszczenie

Condensation of 1,1-dimethyl-3,4-diphenyl-2,5-bis(*p*-tolylhydroxymethyl)silole with pyrrole and *p*-tolylaldehyde did not form the expected 21,21-dimethyl-2,3-diphenyl-5,10,15,20-tetra(*p*-tolyl)-21-silaporphyrin, but rather its reduced derivative, 21-silaphlorin, which contains a tetrahedrally hybridised C5 carbon atom. Attempts to trap 21-silaporphyrin resulted in the serendipitous discovery of a unique transformation of 21-silaphlorin into a non-aromatic isomer of 2,3-diphenyl-5,10,15,21-tetra(*p*-tolyl)-carbacorrole (*iso*-carbacorrole). This novel carbaporphyrinoid contains a cyclopentadiene ring embedded in a tripyrrolic framework. This transformation of 21-silaphlorin to *iso*-carbacorrole, carried out under oxidative conditions, involves extrusion of dimethylsilylene accompanied by migration of the C_{meso}-(*p*-tolyl) unit to create a cyclopentadiene ring directly linked to the adjacent pyrrole through a tetrahedral carbon atom. Insertion of silver or copper ions into *iso*-carbacorrole gave two structurally related organometallic complexes of “true” carbacorrole in which the metal(III) ions are bound by three pyrrolic nitrogen atoms and a tetrahedrally hybridised C21 atom of the cyclopentadiene moiety. In the presence of oxygen, the silver(III) carbacorrole undergoes internal oxidation to 21-oxacorrole. The structure of silver(III) carbacorrole was determined by X-ray crystallography. The C21 atom was found to have a tetrahedral geometry. The Ag□C(sp^3) (2.046(5) Å) bond length is similar to that in silver(III) carbaporphyrinoids in which a trigonal carbon atom coordinates to the metal ion. Density functional theory was applied to model the molecular and electronic structure of 21-silaphlorin and feasible isomers of carbacorrole. The total energies (kcal mol^{-1} vs. *iso*-carbacorrole), calculated at the B3LYP/6-31G**//B3LYP/6-31G* level for carbacorrole, *iso*-carbacorrole, vacataporphyrin and cyclobutadienephlorin, demonstrate the energetic preference for *iso*-carbacorrole.

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