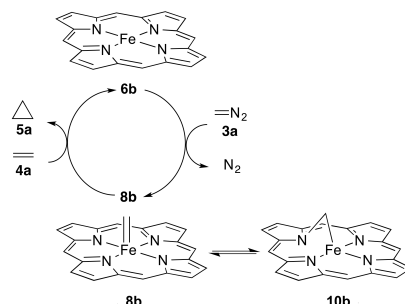


MULTIPLE OXIDATION AND SPIN STATES IN THE CYCLOPROPANATION OF OLEFINS CATALYZED BY FE- PORPHYRIN COMPLEXES

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Cyclopropane derivatives are important building blocks for the chemical synthesis of many valuable compounds, including natural products and biologically active species.^[1] Catalyzed stereocontrolled [2+1] cycloaddition between olefins and carbenes, or carbene precursors, is one of the most convenient methods for the synthesis of cyclopropanes.^[2] Given the instability of carbenes, diazocompounds are used as suitable carbene precursors.^[3] In this work, the mechanism of the cyclopropanation of alkenes with diazocompounds catalysed by Fe^{II}-porphyrin complexes has been investigated using DFT methods.^[4] It is found that the catalytic cycle involves triplet, quintet, and singlet states. Reaction of triplet Fe^{II}-porphyrin complexes with diazocompounds leads to axial and bridged Fe^{II}-carbene complexes. The former type is favored at the singlet state and the latter is the most stable one at higher spin states. The second key step of the reaction consists of the [2+1] cycloaddition of the axial Fe^{II}-carbene complex to yield the corresponding cyclopropane. Both formation of the Fe^{II}-carbene complex and the [2+1] cycloaddition occur on the singlet hypersurface. Several minimum energy crossing points ensure the kinetic and thermodynamic feasibility of the reaction. The reported mechanism is compatible with the observed trans selectivity.



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