

The Encapsulation Chemistry of Coordination Cages

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Inorganic Literature Seminar

October 5, 2004

Zeolites and enzymes are two classic examples of catalytic chemistry occurring in an encapsulated environment.¹ The restricted space of the clefts and pockets of enzymes and the channels and cages of zeolites induce desirable catalyst characteristics such as the molecular recognition of substrates, enhanced reaction rates, and the production of a single isomer of a given compound. These characteristics are achieved through the defined structure, the placement of functional groups, and the reactive metal centers within these structures. Recently the list of materials capable of performing reactions within an encapsulated environment has grown to include molecular coordination structures. Molecular squares synthesized by Hupp along with coordination cages synthesized by Raymond, Fujita, and Reek have shown substrate selectivity, enhanced rates for organic reactions, and the ability to produce a single isomer of a given compound.

The first class of catalytic encapsulation chemistry involves reactions which occur within coordination cages, but proceed without the presence of a reactive metal center. Fujita's palladium nanocage and nanocone (Figure 1) have been shown to perform cavity-directed synthesis of a variety of organic and inorganic reactions such as the alkoxy silane polycondensation, [2+2] photodimerization, [2+4] cycloaddition, and alkane oxidation.² Of particular interest are the [2+2] photodimerization reactions.^{3,4} Within the restricted volume of the cage the dimerization of compounds such as acenaphthylene afforded only the less sterically demanding syn conformation of the dimer. The cage has also exhibited substrate selectivity when the cross-dimerization of acenaphthylene and 5-ethoxynaphthoquinone was performed within the coordination structure. Only the hetero-cross dimer of the acenaphthylene and 5-ethoxynaphthoquinone was formed and the production of either of the homo-dimers was not detected.

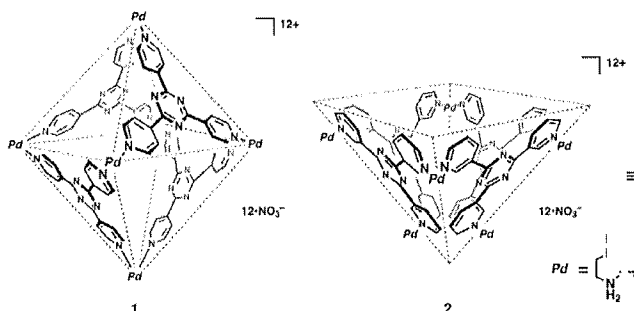


Figure 1: Structure of Fujita's palladium cage and cone with the triazine linker (Pd_6L_4)³

Other coordination cages such as Raymond and Bergman's coordination tetrahedron (Figure 2) have been shown to catalyze organic reactions such as the aza-Cope rearrangement.⁵ The restricted space of the coordination tetrahedron preorganized

the enammonium substrate into a chair-like conformation which then underwent sigmatropic rearrangement.

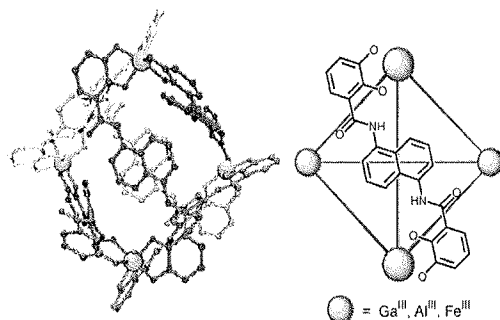


Figure 2: Structure of Raymond's tetrahedron with the catecholamide linker (M_4L_6)¹⁰

The second class of catalytic encapsulation chemistry involves reactions which occur within coordination cages, but proceed *with* a reactive metal center present. The first example of such a compound was reported by Hupp⁶ where a reactive Mn (III) porphyrin epoxidation catalyst was coordinated to the interior of a molecular square (Figure 3). This supramolecular catalyst was not only resistant to degradation, but also showed substrate selectivity. Rhodium hydroformylation and palladium Heck coupling catalysts have been encapsulated inside an array of three porphyrin units by Reek (Figure 3).^{7, 8} This catalyst has shown enhanced rates and selectively yielding branched products over linear products.

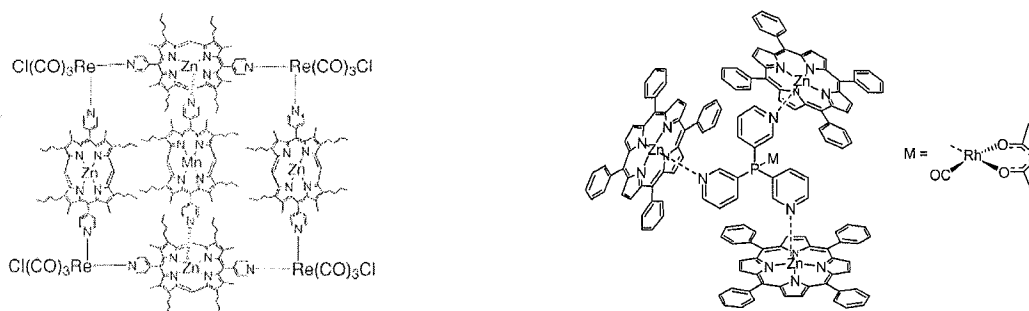


Figure 3: The structure of Hupp's molecular square for epoxidation catalyst⁶ and Reek's encapsulated rhodium catalyst⁷

Raymond and Bergman were able to encapsulate a range of potential metal catalysts within their chiral coordination tetrahedron (Figure 2).⁹ C-H bond activation of aldehydes with modest diastereoselectivity has been observed after the encapsulation of an iridium precursor.¹⁰

Coordination cages with their defined interior cavities can exhibit selectivity towards certain substrates and as a result are emerging as potential catalysts. The encapsulation chemistry which occurs in these coordination cages has shown substrate

selectivity, enhanced rates for organic reactions, and the ability to produce a single isomer of a given compound.

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