



## Digest paper

## Recent developments of cavitand-recessed type metal catalysts



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## ABSTRACT

Metal catalysis inside cavitand space is an emerging field that achieves chemical reactions that were previously unthinkable in bulk solution and causes selectivities not possible heretofore. As the synthetic ways of making metal centers embedded in the cavitand hollows become more simply developed, the catalytic behaviors are gaining increased attention. This Digest will outline catalytic cavitands that have metal centers definitely positioned in the interior of the hemispherical molecules, with emphasis on reports published in the past few years. Specifically, the following targets and approaches are discussed: resorcin[4]arenes, cyclodextrins, and cyclotrimeratrylenes (hemicryptophanes).

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In 1982, Donald J. Cram who was awarded the Nobel Prize in chemistry in 1987, stated the meaning of term ‘cavitand’ as follows,<sup>1</sup> “We propose the class name *cavitand* for synthetic organic compounds that contain *enforced cavities* large enough to accommodate simple molecules or ions.” Since then, researches regarding to organic cavitand scaffolds have continuously made progress from the supramolecular point of view. Today, there are primarily five classes of the cavitand platforms: calixarenes, resorcinarenes, cyclotrimeratrylenes, cucurbiturils, and cyclodextrins.<sup>2</sup> We chemists have synthetically functionalized these platforms to set up molecular diversity, which enables us to make investigation of multiple chemical areas.<sup>3,4</sup>

As one of those areas, there is a field of organometallic chemistry, chemistry that mainly addresses homogeneous transition metal catalysis. The metal catalysis has, of course, been well developed over the past decades. Nowadays its catalytic protocols are indispensable for modern synthetic organic chemistry, whereas it still awaits full accomplishment from the viewpoint of green chemistry: more selective, more efficient, and more reactive catalysts are strongly desirable.<sup>5</sup> For that reason we have a means in strategies of the mind, to mimic metallo-enzymes. Mother Nature creates enzymes that have incredibly marvelous catalysis and serve as well-organized chemical transformation machines. For example, nitrogenase is a representative metal complex enzyme that catalyzes the reduction of atmospheric nitrogen to ammonia under ambient temperature.<sup>6</sup> Its breathtakingly beautiful function

is an excellent teacher for all time: we students should learn and follow the essence of mechanism.

Fortunately for us, enzymes have strong resemblances in two points to supramolecular cavitands.<sup>7</sup> One, enzymes are basically capable of having catalyst centers directed inwardly toward their hydrophobic pockets. Two, the hydrophobic pockets are not tightly sealed so that substrates can readily sample the space, enter and leave. For the first point, cavitands are endowed with gently curved concaves large enough to embrace metal catalyst centers. For the second point, cavitands are originally half open so that guests readily come and go. If these are embodied in the cavitand derivatives as tangible structures, we can provide *definitely cavitand-recessed type metal catalysts* possessing even just a little attribute of metallo-enzymes.

However, such type of the metallic cavitands has been underdeveloped. Two shortcomings provide chemists a continuing challenge. The first problem is the synthetic difficulty to prepare functionalized cavitands even in laboratory-scale. The second is hardships in the synthesis of metal hybrid cavitands in which inwardly directed functionality acts as a supporting ligand to make a complex with transition metals. 50 years have already passed since supramolecular chemistry began,<sup>8</sup> whereas efforts overcoming these drawbacks have been less successful. Here, major challenges remain.

The purpose of this Digest is to focus on rare complexes that have metal centers *definitely at the cavitand recesses* for catalytic use. For the sake of brevity, we have chosen to focus on the following three cavitands, resorcin[4]arenes, cyclodextrins, and cyclotrimeratrylenes (hemicryptophanes) illustrated in Fig. 1; a

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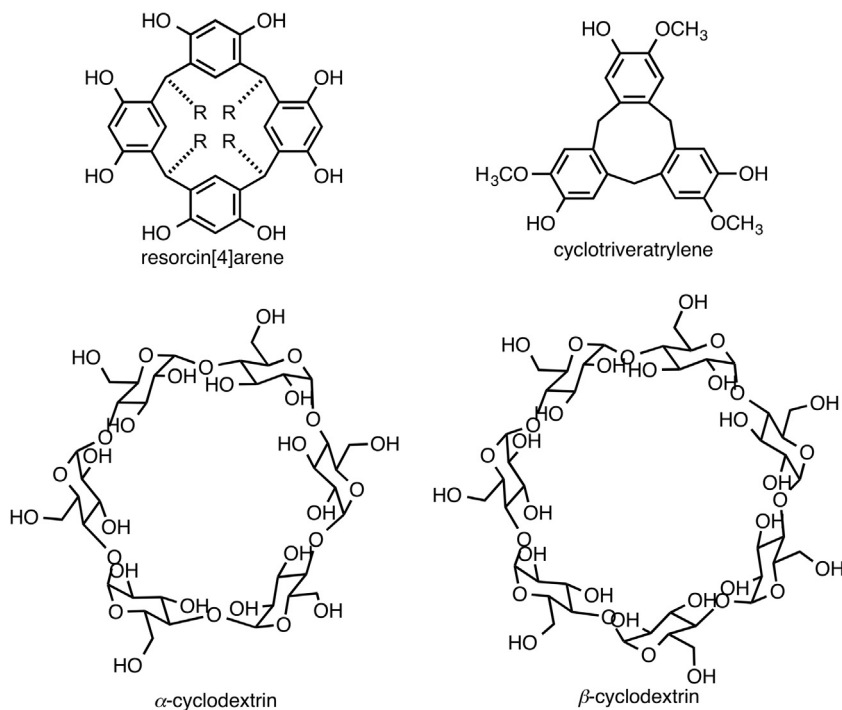


Fig. 1. Three cavitand platforms of resorcin[4]arene,  $\alpha$ - and  $\beta$ -cyclodextrins, and cyclotriveratrylene.

gradual but steady progress in refining these three metallo-catalytic cavitands has been made for the last decade. A full discussion of development around calixarenes, that are flexible compared to other four rigid container frameworks, is best dealt with elsewhere.<sup>9</sup> The chemical reactions catalyzed by cucurbiturils are not in the focus in this Digest, because it is still difficult to definitely put catalytic metal centers in the concave surface.<sup>10,11</sup>

*Resorcin[4]arene-recessed metal catalysts by covalent anchoring.* The resorcin[4]arene scaffold has octanol substructure, which enables us to build up resorcin[4]arene-based cavitands with inwardly directed functional group. We chemists imagine that the 'introvertedly' functional group is up in the interior space toward the tapered end or flanked walls. The reliable method of introvertedly anchoring metal centers to the cavity recess is to

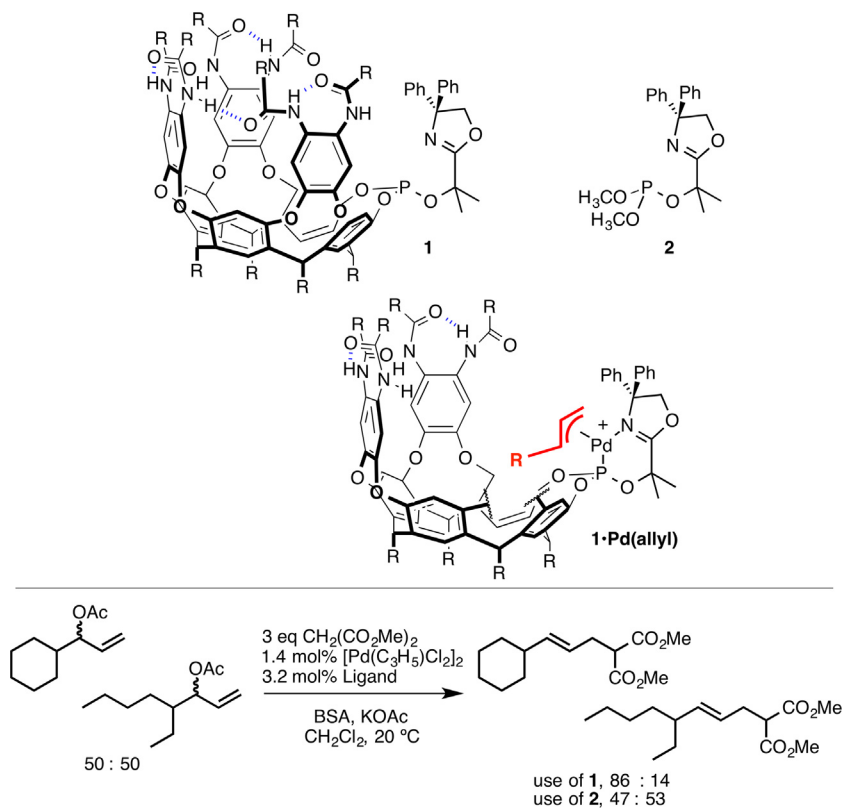


Fig. 2. Palladium-catalyzed allylic alkylation reactions were demonstrated through a use of **1** or **2**. (BSA: *N,O*-bis(trimethylsilyl)acetamide).

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