

Cage Compounds |Hot Paper|

A Discrete Self-Assembled Pd₁₂ Triangular Orthobicupola Cage and its Use for Intramolecular Cycloaddition

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Abstract: Water-soluble $Pd_{12}L_6$ coordination cage **TC-1** was synthesized by coordination-driven self-assembly of symmetrical tetrapyridyl donor **L** with 90° ditopic acceptor *cis*-[Pd(NO₃)₂(tmeda)] [tmeda = *N*,*N*,*N'*,*N'*-tetramethylethane-1,2diamine]. The Pd₁₂L₆ coordination assembly is an uncommon example of a coordination cage having triangular orthobicupola-like geometry. It was characterized by multinuclear NMR spectroscopy, ESI-MS, and single-crystal X-ray diffraction. Self-assembly of a tetratopic donor with a *cis*-blocked 90° ditopic acceptor generally yields tri-/tetra-/hexagonal barrels or closed cubic cages. However, in the present case the donor and acceptor are arranged in an unusual fashion to generate an orthobicupola geometry in which two triangular cupola share a common irregular hexagonal face. The cage was used to perform intramolecular cycloaddition reactions of *O*-propargylated benzylidinebarbituric acid derivatives in nitromethane. Several penta-/tetracyclouracil derivatives were synthesized through cage-catalyzed [4+2] cycloaddition reactions in a concerted manner with good to high conversion under mild reaction conditions, whereas in the absence of cage **TC-1** similar reactions led to lower conversion to the cyclized products in organic solvent. This approach is of particular importance compared to the literature reports on the synthesis of similar compounds under hightemperature reflux conditions with high catalyst loading.

The inherent strongly directional nature of metal-ligand coordination bonds and the versatility of available organic donors

have led to several molecular architectures with predesigned

Introduction

Utilization of weak non-covalent interactions to modulate complex biochemical processes is well established in nature. In enzymes such interactions act through a substrate-binding pocket called the active site.^[1] This strategy has inspired many synthetic chemists to design new supramolecular structures with inner cavities that can mimic their functions.^[2] The inner cavity of the supramolecular architecture typically accelerates the reaction of bound reactants through proximity effects, which greatly increase the local concentration of the substrates (the effective molarity) by decreasing the entropy of the reactants and/ or through preorganization of the reactants in the correct orientation to react, which is reminiscent of enzyme pocket.^[3] In this endeavor, several molecular containers with well-defined cavities have been reported so far.^[4,5]

In the last two-decades metal-ligand coordination-driven self-assembly has emerged as a promising strategy to design and engineer numerous discrete 2D and 3D architectures.^[6]

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D	Supporting information and the ORCID identification number(s) for the au- thor(s) of this article can be found under: https://doi.org/10.1002/chem.201803039.

Chem. Eur. J. 2018, 24, 13938-13946

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shapes, sizes, and functionality. The reversibility of the metalligand coordination provides for thermodynamic control over the self-assembly process, which allows self-correction to form the thermodynamically most stable architecture in quantitative yield. Barrel-shaped discrete open-shell architectures with windows of suitable size are of interest for both easy ingress and egress of large guest molecules.^[7] For this reason, purely organic barrels have been extensively used in molecular transport, catalysis, and sensing.^[8] However, very few examples of metallosupramolecular structures with barrel-like structures are known in the literature, and their applications are largely unexplored.^[9] The M_{2n}L_n-type barrels have been synthesized by the combination of *cis*-blocked Pd^{II} or Pt^{II} complexes having two available coordination sites with tetratopic N-donor ligands in 2:1 stoichiometric ratio. Most of the coordination barrels reported so far are M₈L₄ and M₆L₃ assemblies with square-prismatic and trigonal-prismatic geometries, respectively.^[10] To the best of our knowledge, only a few examples of M_{2n}Ln barrels with more than eight metal centers have been reported so far, and these include a hexagonal $Pt_{12}L_6$ complex reported by $us^{[11]}$ as well as $Pt_{10}L_5$ and $Pt_{16}L_8$ reported by others.^[12] Herein, we report the formation of a water-soluble Pd₁₂ cage, which is the first example of a triangular orthobicupola coordination architecture (Scheme 1) of Pd^{II} obtained by coordination self-assembly. This cage with unique structural topology was ob-