Synthesis of Metal Ligands for Asymmetric Catalytic Reactions of *C*$_3$-Symmetric Cage-Shaped Phosphites.

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Asymmetric metal catalysis for enantioselective synthesis which facilitates the development of pharmaceuticals, agrochemicals, and flavors is flourishing developing field in modern organic chemistry. Designing chiral metal ligands has been a common methodology to achieve high enantioselectivity. Phosphite-containing ligands have emerged as suitable ligands for several asymmetric synthesis reactions such as asymmetric conjugate addition, asymmetric hydrogenation and asymmetric hydroformylation. [1]

In our laboratory, various types of cage-shaped complex have been synthesized and used as Lewis acid catalysts. In 2019, we reported the synthesis of cage-shaped aluminum aryloxides **1**Al·py (Figure **1**A) and their application to Lewis acid catalyst for stereoselectivity glycosylation reaction.[2] In 2017, synthesis of cage-shaped borate **2**B (Figure **1**B) has been reported, and it can be used as chiral Lewis acid catalyst for asymmetric allylation by allyltributylstannane to give the product with high enantiomeric excess (90% *ee*.).[3]

In this work, we transform the central atom from aluminum or boron to phosphorus. A cage-shaped phosphite **3**P (Figure **1**C) was designed and synthesized as a Lewis based metal ligand with a unique *C*$_3$-symmetric structure composed of three homochiral binaphthol moiety.

In addition, the application of cage-shaped phosphite has been investigated. Cage-shaped phosphite **3**P as a chiral metal ligand has been applied to Rh-catalysis asymmetric conjugate addition. It gives the product with high yield (80%) and excellent enantiomeric excess (94% *ee*), when cyclohexene-1-one as *α, β*-unsaturated substrate was used for conjugate addition with phenylboronic acid.

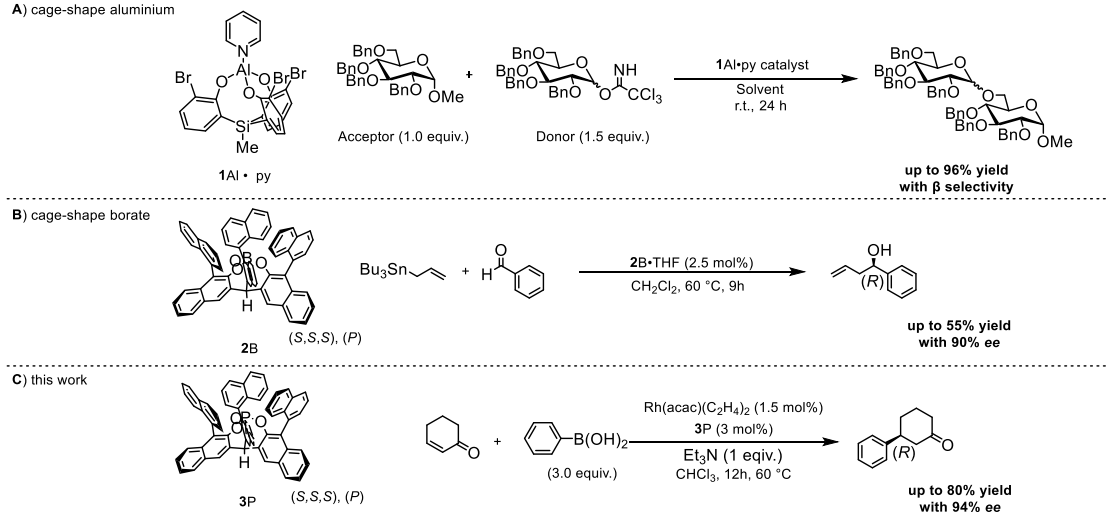

Figure 1. Cage-shaped complex. A) The cage-shaped aluminium aryloxides (**1**Al·py) applied in stereoselectivity glycosylation; B) The cage-shaped borate (**2**B) applied in asymmetric allylation; C) The cage-shaped phosphite (**3**P) applied in Rh-catalysis asymmetric conjugate addition.

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