D. URAGUCHI, H. SASAKI, Y. KIMURA, T. ITO, T. OOI* (NAGOYA UNIVERSITY, JAPAN) Molecular Design, Synthesis, and Asymmetric Catalysis of a Hexacoordinated Chiral Phosphate Ion *J. Am. Chem. Soc.* **2018**, *140*, 2765–2768.

Enantioselective Cyclization by a Hexacoordinated Chiral Hydrogen Phosphate

$$R^{1} = \text{Me, OMe, Cl} \qquad R^{2} = \text{Alk} \qquad \begin{array}{c} \text{1.H.(urea)}_{2} \\ \text{(2 mol\%)} \\ \text{CH}_{2}\text{Cl}_{2} \\ -90 \text{ °C} \\ \end{array} \qquad \begin{array}{c} \text{R}^{1} \\ \text{II} \\ \text{N} \\ \text{N} \\ \text{R}^{2} \\ \text{Ph} \\ \end{array} \qquad \begin{array}{c} \text{R}^{3} \\ \text{Ph} \\ \text{N} \\ \text{N} \\ \text{Ph} \\ \end{array} \qquad \begin{array}{c} \text{R}^{3} \\ \text{Ph} \\ \text{R}^{3} \\ \text{Ph} \\ \text{N} \\ \text{O} \\ \text{CF}_{3} \\ \end{array} \qquad \begin{array}{c} \text{R}^{3} = 3,5 \cdot \text{Ph}_{2}\text{C}_{6}\text{H}_{3}\text{CH}_{2} \\ \text{H} \\ \text{er from 93.5:6.5 to 98:2} \\ \end{array}$$

Selected examples:

Catalyst synthesis:

Significance: The Ooi group reports a Pictet–Spengler-type cyclization catalyzed by the Brønsted acid 1·H. The presented chiral hexacoordinated phosphate ion consists of two N,N,O-tridentate backbones, including 1,2-diphenylethylenediamine as a readily available chiral source. The catalyst is prepared by deprotonation of a phenol followed by cation exchange. The authors obtained a single-crystal X-ray structure of 1·HNEt₃ which confirmed its octahedral P(V) core.

Comment: The authors demonstrate the catalytic activity of **1** as hydrogen phosphate. Although the substrate scope is limited, it is noteworthy that the hexacoordinated phosphate can indeed control the enantioselectivity. More mechanistic studies and control experiments would be highly appreciated to further understand and expand the presented transformation.

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Category

Organo- and Biocatalysis

Key words

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phosphates

Pictet-Spenglertype cyclization

