

Catalyst Control Over Pentavalent Stereocentres

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A plethora of catalytic methods have been developed to address one of two configurations of tetravalent stereocenters.¹ Conversely, achieving control over high-valent stereocenters has proven to be a persisting challenge. Pentavalent stereocenters, characterized by a fifth moiety attached to the central atom, encode an extended stereochemical space beyond the classical Le Bel–van 't Hoff stereo-isomerism^{2,3} ($>2^n$), which results in having more than two stereoisomers per one stereocenter. In this work, a catalytic method allowing the selection of configurations in pentavalent stereocenters was developed. A bifunctional iminophosphorane thiourea catalyst⁴ enables precise control over enantio- and diastereomers emerging from a single stereocenter of pentavalent phosphoranes, yielding desired dioxophosphoranes with excellent yield and selectivity (up to 99% yield, 96:4 e.r. and 99:1 d.r.). Stereodivergent catalysis allows selective access to each different diastereomeric state of the pentavalent phosphoranes, rendering the expanding stereochemical space of high-valent main group species selectively addressable.⁵

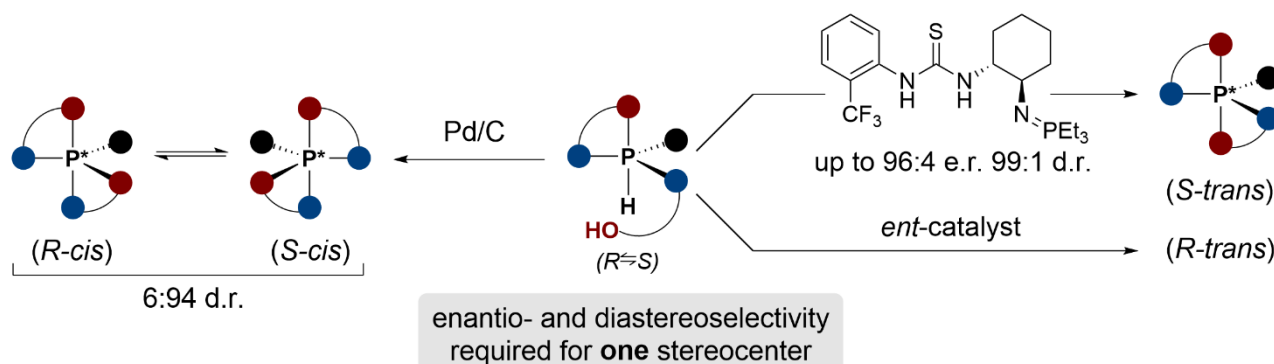


Figure 1. Catalyst Control Over Pentavalent Stereocentres.

1 E. N. Jacobsen, A. Pfaltz, H. Yamamoto, *Comprehensive Asymmetric Catalysis*, Springer, **1999**.

2 J. A. Le Bel, *Bull. Soc. Chim. Fr.*, **1874**, 22, 337.

3 J. H. Van 't Hoff, *Arch. Neerl. Sci. Exactes Nat.*, **1874**, 9, 445.

4 M. Formica, D. Rozsar, G. Su, A. J. M. Farley, D. J. Dixon, *Acc. Chem. Res.*, **2020**, 53, 2235.

5 A. Budeev, J. Dong, D. Häussinger, C. Sparr, *Nat. Commun.*, **2023**, 14, 8013. (Highlighted in *Chimia: Chimia*, **2024**, 78, 162).