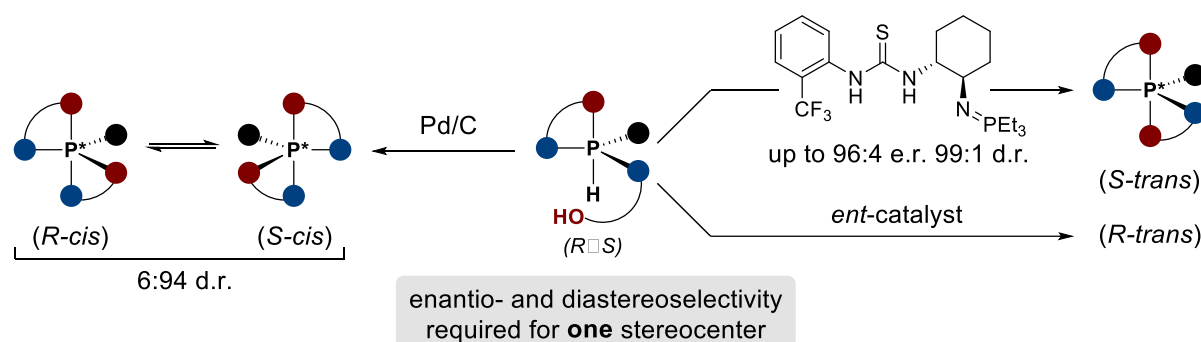


Catalyst Control Over Pentavalent Stereocenters

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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 stereoisomerism^[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 catalyst^[4] 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]

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