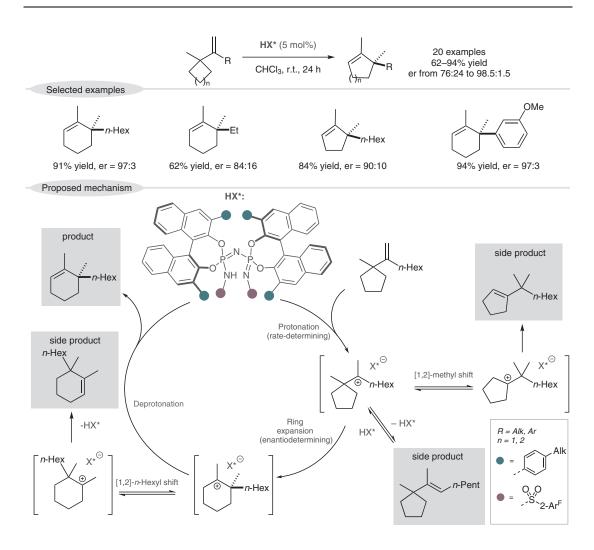
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## Catalytic Enantioselective Wagner–Meerwein Rearrangement of Alkenyl Cycloalkanes



**Significance:** List, Tantillo and co-workers report catalytic asymmetric cationic shifts of purely aliphatic hydrocarbons enabled by IDPi catalysis. Both four- and five-membered ring substrates bearing aromatic, linear and branched alkyl substituents delivered the corresponding cycloalkene products in excellent yields and enantioselectivities. Calculations revealed the ring expansion step to be enantiodetermining in which C-H···O hydrogen bonds are crucial for enantioselectivity.

**Comment:** Until recently, asymmetric Wagner–Meerwein reactions of purely aliphatic hydrocarbon substrates were unexplored, since the absence of functional groups limits the specific substrate-catalyst interactions. Additionally, non-stabilized carbocation intermediates are challenging in terms of enantiodifferentiation and reactivity control. These challenges were addressed by generation of a stabilized carbocation within the sterically and electronically fine tuned IDPi anion pocket.

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