Highly Enantioselective Ruthenium / PNNP-Catalyzed Imine Aziridination: An Unprecedented Mechanism Makes it Possible

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Methods of Imine Aziridination

Lewis Acid Activation

CHPh₂Ar + CHPh₂Ar → CHPh₂ArH + CHPh₂ArH

Brønsted Acid Activation

CHPh₂Ar + CHPh₂Ar → CHPh₂ArH + CHPh₂ArH

Bredsted Acid Activation

CHPh₂Ar + CHPh₂Ar → CHPh₂ArH + CHPh₂ArH

Ruthenium(III) / PNNP Catalysts

For a study of the equilibria in solution, see: Schotes, C.; Ranocchiari, M.; Mezzetti, A. Organometallics 2011, 30, 3596.

Imine Aziridination: Substrate Scope

Mechanistic Studies

Resting Species during Catalysis:

A Diazoalkane Complex

<table>
<thead>
<tr>
<th>Diazoalkane Activation</th>
<th>Carbene Complex</th>
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<tbody>
<tr>
<td>R₁ + Ar</td>
<td>R₁ + Ar</td>
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<tr>
<td>R₂ + Ar</td>
<td>R₂ + Ar</td>
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</tbody>
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Complexes 8 and 9 were characterized in solution by NMR spectroscopy using 13C and 15N-labeling.

Diazoealkane Activation and Reaction Mechanism

The coordination to ruthenium destabilizes the HOMO of EDA (4-electron node).

Hence, EDA becomes more nucleophilic and reacts with the imine, a weak electrophile.

Nonproductive branch

Decay to carbene complex must be inhibited to optimize the chemoselectivity to aziridines!

The carbene complex 7 gives diethyl maleate, ...

... but does not react with the imine, because its electrophilicity is too low.